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# BAND THEORY, VALENCE BOND AND TIGHT-BINDING CALCULATIONS

by

Per-Olov Löwdin

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Uppsala University, Uppsala, Sweden

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# BAND THEORY, VALENCE BOND AND TIGHT-BINDING CALCULATIONS*

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## CONTENTS

# ERRATA

p. 4, reference 8: J.C. Slater, Phys. Rev. 51, 846 (1937).

p. 7, 3 lines below eq. (13): $0 \leq \mu_\nu \leq G-1$ .

p. 8, eq. (16): In the exponential factor read "$2\pi i\, \mathfrak{k}\cdot\mathfrak{m}$".

p. 9, line 11 from the bottom: Read " ... fact, that the eigenvalues $\epsilon(\mathfrak{k})$ ...

p. 28, 5 lines below reference 63: Read "... approach the correct value for $R = \infty$. The general ... "

p. 31, reference 70: W. Heitler and F. London, Z. Physik 44, 455 (1927).

p. 45, 3 lines above eq. 66: Read "... whereas the orthonormality condition $\mathfrak{S}^\dagger \mathfrak{S} = \mathbf{1}$ leads to ... "

p. 71, 1 line above eq. (103): Read " ... satisfying $(H-E)\Psi = 0$ , one has ... "

## ABSTRACT

In the theory of the electronic structure of crystals, the fundamental features of the band theory, the valence bond method, and the tight-binding approximation are reviewed. The band theory is studied on the basis of the Hartree-Fock scheme, and the Bloch functions are formed by a projection technique. The main methods for calculating Hartree-Fock functions in a solid are briefly discussed. The advantages and disadvantages of the band theory and the valence bond method are emphasized, and special attention is paid to the correlation error.

In connection with the tight-binding approximation, the importance of the continuum part and of the approximate linear dependencies is stressed. It is shown that a complete orthonormal set of translationally connected atomic orbitals may be constructed as a convenient basis for this approach. The implication of the virial theorem in interpreting the cohesive properties of the ionic crystals is further emphasized.

Some recent refinements of band theory are then discussed. It is shown that a large part of the correlation error can be removed by permitting "different orbitals for different spins". This leads to a scheme intermediate between band theory and valence bond method and, by means of a single parameter, one can obtain an essential lowering of the energy curve and the correct asymptotic behaviour for separated atoms or constituents. This approach may be generalized to an extension of the Hartree-Fock scheme, where the total wave function is defined as a projection of a Slater determinant.

The band theory can be further refined and connected to the exact solution of the many-electron Schrödinger equation of the crystal by means of an extension of the self-consistent-field scheme, utilizing the so-called reaction operator here exactly defined by means of a simple partitioning technique. The various types of self-consistent field theories are finally compared.

## 1. INTRODUCTION

The quantum theory of the electronic structure of crystals has historically been developed essentially along two main lines based on band theory and valence bond method, respectively. Both approaches are to a certain extent approximate, and the former seems to be more appropriate for describing conductors and semi-conductors, whereas the latter seems particularly convenient for studying insulators. Actually, both methods are needed in order to understand the general properties of crystals and their electric, magnetic, optical, cohesive, elastic, and thermal behaviour, and the fundamental problem is then how they could be combined and refined to give any accuracy desired.

In this survey, the recent progress in this field will be briefly reviewed. The advantages and disadvantages of band theory and valence bond method will be discussed, and the nature of the approximations and errors involved will be investigated. Special attention is given the so-called tight--binding approximation, and the importance of the virial theorem in interpreting energy results in crystal theory will be emphasized.

A simple generalization of band theory to include correlation effects will be described. It will be shown that the main advantages of band theory and valence bond method may be further enhanced and the disadvantages and errors partly removed by a synthesis of the two ideas, which may be characterized as a band theory with different orbitals for different spins.

The relation between band theory and the exact many-electron theory of a crystal will be further studied. It will be shown that, in connection with the exact description, there exists a one-electron model based on a general self-consistent-field scheme which may be considered as an extension of Brueckner's generalization of the Hartree-Fock approximation. This result is obtained by means of the exact reaction operator which is here derived by a partitioning technique offering a simple and forceful alternative to the otherwise used infinite-order perturbation theory.

In conclusion, the various approaches will be compared and discussed. By means of density matrices, it will be shown that, independent of the way one is solving the Schrödinger equation, certain aspects of the one-electron band theory will be preserved also in the exact many-electron theory, for

instance the concepts of reduced wave vector $\mathbf{k}$, effective mass, etc.

Since we are here mainly interested in the electronic structure of crystals, we will throughout the entire paper assume that the nuclei are fixed in the positions characteristic for the lattice under consideration, and that the nuclear coordinates may be treated as parameters in the electronic wave function (Born-Oppenheimer approximation).

## 2. FUNDAMENTS OF BAND THEORY

### (a) Hartree-Fock Approximation

The band theory of crystals is physically built on the independent-particle-model, according to which each electron in a many-electron system moves under the influence of the outer field and the "average" field of all the other electrons [1]. For each electron, there exists an effective

[1] N. Bohr, Proc. London Phys. Soc. 35, 296 (1923).

Hamiltonian $H_{eff}$ and a Schrödinger equation of the form

$$\mathcal{H}_{eff}(1)\,\psi_k(1) = \epsilon_k\,\psi_k(1) , \tag{1}$$

where $\psi_k(x_1)$ is a spin-orbital, $x_1 = (r_1, \zeta_1)$ is the space-spin coordinate of electron 1, and $\epsilon_k$ the corresponding one-electron energy. In the Hartree-Fock scheme [2], the total electronic wave function $\Psi$ is approximated by a

[2] D.R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928); V. Fock, Z. Physik 61, 126 (1930); J.C. Slater, Phys. Rev. 35, 210 (1930); P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930); 27, 240 (1931).

single Slater determinant:

$$\Psi = (N!)^{-1/2} \det\{\psi_1, \psi_2, \ldots \psi_N\} , \tag{2}$$

where $\psi_1, \psi_2, \ldots \psi_N$ are the occupied spin-orbitals, which are assumed to form an orthonormal set. The effective Hamiltonian is represented by the expression

$$\mathcal{H}_{\text{eff}} = \frac{1}{2m} p_1^2 - e^2 \sum_g \frac{Z_g}{r_{1g}} + e^2 \int dx_2 \frac{\rho(x_2, x_2) - \rho(x_2, x_1) P_{12}}{r_{12}}, \tag{3}$$

where the first term is the kinetic energy, the second the attraction potential between electron 1 and the nuclei g, whereas the last term is the above--mentioned "average" potential from all the other electrons. The quantity $\rho$ is the Fock-Dirac density matrix:

$$\rho(x_1, x_2) = \sum_{k=1}^{N} \psi_k(x_1) \psi_k^*(x_2), \tag{4}$$

which satisfies the basic relations $\rho^2 = \rho$, $\mathrm{Tr}(\rho) = N$. The operator $P_{12}$ is an exchange operator with respect to the electronic coordinates $x_1$ and $x_2$, and the corresponding exchange potential has hence a non-local character [3]. The spin-orbital energies $\epsilon_k$ have a physical meaning in connection with the first ionization potentials [4] and, to a certain extent, they may be used also in studying the excitation energies [5].

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3) For the approximation of the exchange potential by a local potential, see J.C. Slater, Phys. Rev. 81, 385 (1951); V.W. Maslen, Proc. Phys. Soc. A69, 734 (1956); P.O. Löwdin, Phys. Rev. 97, 1474 (1955); p. 1487 f.

4) T. Koopmans, Physica 1, 104 (1933).

5) See e.g. P.O. Löwdin, Phys. Rev. 97, 1490 (1955), and references there.

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The Hartree-Fock equations (1) are a system of non-linear integro--differential equations connected with an eigenvalue problem which are solved by the "self-consistent-field" (SCF) procedure. This may be indicated by the diagram

$$\rho \longrightarrow \mathcal{H}_{\text{eff}} \longrightarrow \{\psi_k\} \longrightarrow \rho \qquad (5)$$

and, after being started by an initial estimate of $\rho$ or $\{\psi_k\}$, the cycle is repeated until the procedure becomes "self-consistent", i.e. no further changes occur in the significant figures when the cycle is repeated. The eigenvalue problem (1) has in the atomic case [6] been solved by numerical integration, and this approach has also been applied to crystals in the cellular method [7] and in the augmented plane wave method [8]. The expansion method by Ritz [9] was first applied to the SCF-procedure in connection with molecules [10], but later this technique has proven to be very useful also in the cases of atoms and crystals.

6) For a survey of the atomic SCF-calculations, see D.R. Hartree, Repts. Prog. Phys. 11, 113 (1948); "Calculation of Atomic Structures" (John Wiley and Sons, New York 1957); R.S. Knox, Solid-State Physics 4, 413 (Academic Press, New York 1957); P.O. Löwdin, Proc. R.A. Welch Found. Conf. Chem. Res. II. Atomic Structure, 5 (1958).

7) E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

8) J.C. Slater, Phys. Rev. 846 (1937); 92, 603 (1953).

9) W. Ritz, J. reine angew. Math. 135, 1 (1909).

10) C.A. Coulson, Proc. Cambridge Phil. Soc. 34, 204 (1938).

The methods of molecular theory may, in principle, be applied also to crystals, since the latter are nothing but molecules of an immense size characterized by translational symmetry. If one chooses atomic orbitals (AO's) as a basis in Ritz's method, the molecular orbitals (MO's) associated with a specific Hamiltonian may be found by linear combinations of atomic orbitals (LCAO) [11]. In solid-state theory this approach was introduced by

11) F. Hund, Z. Physik 51, 759 (1928); 73, 1 (1931); R.S. Mulliken, Phys. Rev. 32, 186 (1928); 41, 49 (1932); J.E. Lennard-Jones, Trans. Faraday Soc. 25, 668 (1929). For a survey, see R.S. Mulliken, J. chim. phys. 46, 497, 675 (1949).

Bloch [12], and it goes under the name of "tight-binding approximation". The coefficients in the MO-LCAO expansions may be determined so that the molecular orbitals become Hartree-Fock functions by an iteration procedure [13] analogous to (5) and, since the total wave function is approximated by a single Slater determinant or antisymmetrized product (ASP), the entire approach is often denoted by the symbol ASP-MO-LCAO-SCF introduced by Mulliken. Even direct methods for evaluating $\rho$ without the use of $\{\psi_k\}$ have been developed [14].

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12) F. Bloch, Z. Physik 52, 555 (1929); 57, 545 (1929).

13) C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).

14) R. McWeeny, Proc. Roy. Soc. (London) A235, 496 (1956); A237, 355 (1956); Technical Note 61, Uppsala Quantum Chemistry Group (1961), (unpublished).

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The Hartree-Fock scheme may be considered as an approximate method for solving the many-electron Schrödinger equation

$$\mathcal{H}_{op} \Psi = E \Psi \quad , \tag{6}$$

where $\Psi = \Psi(x_1, x_2, \ldots x_N)$ is the many-electron wave function subject to the antisymmetry requirement $P\Psi = (-1)^p \Psi$ corresponding to Pauli's exclusion principle. For a crystal with fixed nuclei, the total Hamiltonian has the form:

$$\mathcal{H}_{op} = e^2 \sum_{g<h} \frac{Z_g Z_h}{r_{gh}} + \sum_{i=1}^{N} \left( \frac{p_i^2}{2m} - e^2 \sum_{g} \frac{Z_g}{r_{ig}} \right) + \sum_{i<j} \frac{e^2}{r_{ij}} \quad , \tag{7}$$

where the first term represents the nuclear repulsion, the second the kinetic energy of the electrons, the third the attraction between the electrons and the nuclei, and the fourth the mutual electronic repulsion. Spin-coupling terms are easily added.

One may solve the eigenvalue problem (6) by means of the variation

principle $\delta \langle H_{op} \rangle_{Av} = 0$. If the total wave function is approximated by a single Slater determinant, this leads to the Hartree-Fock equations (1) with an effective Hamiltonian given by (3). For the ground state, the corresponding total energy $E_{HF} = \langle H_{op} \rangle_{Av}$ is an upper bound to the true eigenvalue $E$, and the energy error $(E - E_{HF})$ or "correlation energy" may be used as a measure of the accuracy of the entire approach. It is hardly necessary to emphasize that the Hartree-Fock energy is not identical with the sum of the spin-orbital energies

$$\int \mathcal{H}_{eff}(1)\, \rho(x_1, x_1')_{x_1'=x_1}\, dx_1 = \sum_{k=1}^{N} \epsilon_k \,. \tag{8}$$

For the Hartree-Fock energy, one may use anyone of the following three formulas:

$$E_{HF} = e^2 \sum_{g<h} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int p_1^2\, \rho(x_1, x_1')_{x_1'=x_1}\, dx_1 - e^2 \sum_g Z_g \int \frac{\rho(x_1, x_1)}{r_{1g}}\, dx_1 + \frac{e^2}{2} \int \frac{\rho(x_1,x_1)\,\rho(x_2,x_2) - \rho(x_1,x_2)\,\rho(x_2,x_1)}{r_{12}}\, dx_1\, dx_2 = \tag{9}$$

$$= e^2 \sum_{g<h} \frac{Z_g Z_h}{r_{gh}} + \sum_{k=1}^{N} \epsilon_k - \frac{e^2}{2} \int \frac{\rho(x_1,x_1)\,\rho(x_2,x_2) - \rho(x_1,x_2)\,\rho(x_2,x_1)}{r_{12}}\, dx_1\, dx_2 = \tag{10}$$

$$= e \sum_{g<h} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2} \sum_{k=1}^{N} \epsilon_k + \frac{1}{4m} \int p_1^2\, \rho(x_1, x_1')\, dx_1 - \frac{e^2}{2} \sum_g Z_g \int \frac{\rho(x_1,x_1)}{r_{1g}}\, dx_1 . \tag{11}$$

where the last form is simply the artithmetic mean of the two first relations. We note that, for crystals, one has to include the nuclear repulsion term in the calculations, since otherwise $E_{HF}$ will become divergent, i.e. no longer proportional to the volume of the crystal [15].

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15) P.O. Löwdin, Advances in Physics 5, 1 (1956), p. 11 f.

## (b) Translational Symmetry

An ideal crystal is characterized by the translational symmetry which is basic for the understanding of its fundamental properties. Let $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ be the primitive translations of the ordinary lattice and $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of the reciprocal lattice, so that $\mathbf{a}_k \cdot \mathbf{b}_l = \delta_{kl}$. The vectors $\mathbf{m} = \mu_1\mathbf{a}_1 + \mu_2\mathbf{a}_2 + \mu_3\mathbf{a}_3$, where $(\mu_1, \mu_2, \mu_3)$ is a triple of integers, connect equivalent points in the ordinary lattice, whereas the vector $\mathbf{K} = i_1\mathbf{b}_1 + i_2\mathbf{b}_2 + i_3\mathbf{b}_3$ for integer $(i_1, i_2, i_3)$ connect equivalent points in the reciprocal lattice. Let further $T_1, T_2, T_3$ be the translational operators connected with the primitive translations $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ respectively, and defined by the relation

$$T_\nu \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a}_\nu) . \tag{12}$$

For the operator $T(\mathbf{m})$ connected with the general translation $\mathbf{m}$ one has $T(\mathbf{m}) = T_1^{\mu_1} T_2^{\mu_2} T_3^{\mu_3}$ .

The treatment of the translational symmetry is greatly simplified, if one introduces the Born-v. Kármán [16] boundary condition:

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16) M. Born and T. von Kármán, Physik. Z. 13, 297 (1912).

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$$\psi(\mathbf{r} + G\mathbf{a}_\nu) = \psi(\mathbf{r}) , \tag{13}$$

where $G$ is a very large integer, which defines the periodically repeated microcrystal. Each microcrystal contains $G^3$ lattice points characterized by the triple $(\mu_1, \mu_2, \mu_3)$, and the inequality $0 < \mu_\nu < G-1$ defines a convenient "ground domain" (G). It follows from (13) that $T_\nu^G = 1$, i.e. the three translations will now be cyclic operators of order $G$ having the eigenvalues $\exp(2\pi i\kappa_\nu/G)$ where $\kappa_\nu$ is an integer. The associated eigenvalue problem is now easily solved by a simple projection technique [17], which does not require any use of group theory. It is shown that one may conveniently label

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17) P.O. Löwdin, Phys. Rev. 97, 1509 (1955); p. 1512; Advances in Physics 5, 1 (1956), p. 56 f.

the simultaneous eigenfunctions to $T_1$, $T_2$, $T_3$ either by the triple of integers $(\kappa_1, \kappa_2, \kappa_3)$ or by the reduced wave vector:

$$\mathbf{k} = (\kappa_1 \mathbf{b}_1 + \kappa_2 \mathbf{b}_2 + \kappa_3 \mathbf{b}_3)/G \quad , \tag{14}$$

$$-G/2 \leq \kappa_\nu < +G/2 \quad , \tag{15}$$

where the inequality (15) defines a ground domain (G) containing $G^3$ points in k-space. The eigenvalue relation may now be written in the form:

$$T(\mathbf{m})\,\psi(\mathbf{k},\mathbf{r}) = \psi(\mathbf{k},\mathbf{r}+\mathbf{m}) = e^{2\pi i\,\mathbf{k}\cdot\mathbf{r}}\,\psi(\mathbf{k},\mathbf{r}) \;. \tag{16}$$

For $\mathbf{m}$ equal to the primitive translations, this gives the famous Bloch condition. The corresponding eigenfunctions may be found by means of the projection operators [17]:

$$O_{\mathbf{k}} = G^{-3} \sum_{\mathbf{m}}^{(G)} e^{2\pi i\,\mathbf{k}\cdot\mathbf{m}}\, T(-\mathbf{m}) \quad , \tag{17}$$

which fulfil the following basic relations:

$$O_{\mathbf{k}}^2 = O_{\mathbf{k}}, \quad O_{\mathbf{k}}^{\dagger} = O_{\mathbf{k}} , \quad O_{\mathbf{k}} O_{\mathbf{l}} = 0 , \; (\mathbf{k} \neq \mathbf{l}) , \tag{18}$$

$$T(\mathbf{m})\, O_{\mathbf{k}} = e^{2\pi i\,\mathbf{k}\cdot\mathbf{m}}\, O_{\mathbf{k}} \;. \tag{19}$$

One has further the "resolution of the identity" $1 = \sum_k O_k$ which implies that every trial function $\Phi(\mathbf{r})$ satisfying the periodicity condition (13) may be resolved into Bloch components, i.e.

$$\Phi(\mathbf{r}) = \sum_{\mathbf{k}}^{(G)} O_{\mathbf{k}}\, \Phi(\mathbf{r}) = \sum_{\mathbf{k}}^{(G)} \Phi(\mathbf{k},\mathbf{r}) \;, \tag{20}$$

which are not only orthogonal but also <u>non-interacting</u> with respect to every operator $\Omega$ which commutes with the translations $T_1$, $T_2$, $T_3$ according to the general formulas

$$\mathbb{O}_{\mathbf{k}}^{\dagger}\,\mathbb{O}_{\mathbf{l}} = 0, \qquad \mathbb{O}_{\mathbf{k}}^{\dagger}\,\Omega\,\mathbb{O}_{\mathbf{l}} = 0 \tag{21}$$

for different reduced wave vectors ( $\mathbf{k} \neq \mathbf{l}$ ). The fundamental relations (17)--(21) are easily verified directly.

<u>Band Structure; Brillouin Zones.</u> - If the integer G characteristic for the microcrystal is very large, the density of points (14) becomes so large that the set may be considered as quasi-continuous. It becomes then possible to replace a summation over $\mathbf{k}$ -space with a corresponding integral

$$V^{-1}\sum_{\mathbf{k}} f(\mathbf{k}) = \int f(\mathbf{k})\,(d\mathbf{k}), \tag{22}$$

where V is the volume of the microcrystal. This quantity enters the formula, since each discrete point in $\mathbf{k}$ -space is associated with the volume $\mathbf{b}_1\cdot(\mathbf{b}_2\times\mathbf{b}_3)/G^3 = 1/G^3\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3) = 1/V$.

We will now consider the spin-orbital energies $\epsilon = \epsilon(\mathbf{k})$ as functions of the quasi-continuous variable $\mathbf{k}$ over the ground domain. The name "band theory" comes actually from the fact, that the eigenvalues show a band structure with the levels situated in certain allowed ranges or "bands" separated by forbidden regions or energy "gaps". The ground domain has here been fixed by the inequality (15), but even other choices are possible and may physically be more convenient.

In order to study the $\mathbf{k}$ -space as a whole, we will now introduce the <u>plane waves</u> $\eta(\mathbf{k},\mathbf{r}) = V^{-1/2}\exp(2\pi i\,\mathbf{k}\cdot\mathbf{r})$ , where $\mathbf{k}$ is a wave vector defined by (14) but with no restriction on the integers $(\kappa_1, \kappa_2, \kappa_3)$. Each $\mathbf{k}$ -value is equivalent to one and only one point $\mathbf{k}_G$ within the ground domain and, since $T_\nu\,\eta(\mathbf{k},\mathbf{r}) = \exp(2\pi i\,\mathbf{k}_G\cdot\mathbf{a}_\nu)\,\eta(\mathbf{k},\mathbf{r})$ , equivalent $\mathbf{k}$ -values are associated with the same translational eigenvalue. All points

in $\mathbf{k}$ -space can hence be divided into $G^3$ sets of equivalent points, and the points within each set may further be arranged linearly after some physical quantity, say $|\mathbf{k}|^2$. Each $\mathbf{k}$ -value would then have its unique place within each series, and ambiguities could occur only when two equivalent points, $\mathbf{k}$ and $\mathbf{k}'$, would have the same absolute value:

$$\mathbf{k}' - \mathbf{k} = \mathbf{K}, \qquad |\mathbf{k}|^2 = |\mathbf{k}'|^2 . \tag{23}$$

These are the equations for the boundaries between the so-called Brillouin zones [18]: the first zone contains apparently all non-equivalent points having

[18] L. Brillouin, Comp. rend. 191, 198, 292 (1930); J. phys. radium (7), 1, 377 (1930).

the smallest value of $|\mathbf{k}|^2$, the second zone contains all non-equivalent points having the second smallest value of $|\mathbf{k}|^2$, etc.. If the points on the boundaries are assigned to the zones in a proper way, each zone contains exactly $G^3$ points with one and only one representative for every set of equivalent points. All zones have the same volume and may be "mapped" on the first Brillouin zone or on the ground domain defined by (15).

The relations (23) are in crystal physics known as the Laue conditions for X-ray diffraction in lattices. The zone structure was introduced by Brillouin in a study of the energy splitting of plane waves by means of a weak periodic potential, which he found caused discontinuities or "energy gaps" at the zone boundaries. These have hence a simple physical meaning.

The band splitting through various types of periodic potentials have been investigated in great detail in a series of special examples chosen so that the corresponding eigenvalue problem could be exactly solved [19].

[19] P.M. Morse, Phys. Rev. 35, 1310 (1930); R. de L. Kronig and W.G. Penney, Proc. Roy. Soc. (London) A130, 499 (1931); H.A. Kramers, Physica 2, 483 (1935); J.C. Slater, Phys. Rev. 87, 807 (1952); F.L. Scarf, Phys. Rev. 112, 1137 (1958); and others.

In the following, we will concentrate our interest on the consequences of the translational symmetry in the Hartree-Fock scheme, and it is then convenient to consider $\epsilon = \epsilon(\mathbf{k})$ as a multi-valued function of the reduced wave vector $\mathbf{k}$ over the first Brillouin zone or over the ground domain (G).

Translations as Constants of Motion. - It is important to observe the difference between a crystal problem based on the assumption of a fixed periodic potential like the previously mentioned models [19] and the Hartree--Fock scheme, where the potential in the effective Hamiltonian (3) depends on the solutions to the eigenvalue problem (1). The latter problem is of a non--linear nature and considerably more complicated. It can be approached by considering the N-electron operator ($\nu = 1, 2, 3$):

$$\mathcal{T}_\nu = \prod_{i=1}^{N} T_\nu(i) = T_\nu(1)\, T_\nu(2) \ldots T_\nu(N) \,, \tag{24}$$

which corresponds to a primitive translation $\mathbf{a}_\nu$ of all electronic coordinates, i.e. to a translation of the electronic cloud as a whole. Since

$$\mathcal{T}_\nu \mathcal{H}_{op} = \mathcal{H}_{op} \mathcal{T}_\nu \tag{25}$$

for the many-electron Hamiltonian (7), the total translation $\mathcal{T}_\nu$ is a normal constant of motion to the many-electron system. This theorem may seem trivial, but it is actually of fundamental importance in both the one-electron--approximation and the exact theory.

It is easily shown that $\mathcal{T}_\nu$ is another cyclic operator of order G, and its eigenvalues and eigenfunctions may hence be derived in the same way as before; see equations (12)-(21). The eigenfunctions may be labelled by means of a total reduced wave vector $\mathbf{K}$ of type (14), restricted to $G^3$ different values by the inequality (15). These eigenfunctions fulfil the generalized Bloch condition

$$\mathcal{T}(\mathbf{m})\, \Phi(\mathbf{K}; x_1, x_2, \ldots x_N) = e^{2\pi i \mathbf{K}\cdot\mathbf{m}}\, \Phi(\mathbf{K}; x_1, x_2, \ldots x_N) \,, \tag{26}$$

where $\mathfrak{T}(m) = \mathfrak{T}_1^{\mu_1}\mathfrak{T}_2^{\mu_2}\mathfrak{T}_3^{\mu_3}$ means a translation of all electronic coordinates a vector $m = \mu_1 a_1 + \mu_2 a_2 + \mu_3 a_3$. The associated projection operators

$$\mathbb{O}_k = G^{-3} \sum_m^{(G)} e^{2\pi i k\cdot m}\, \mathfrak{T}(-m) \tag{27}$$

satisfying the identity $1 = \sum_k \mathbb{O}_k$, may be used to resolve any arbitrary many-electron function $\Phi(x_1, x_2, \ldots x_N)$ into components

$$\begin{aligned} \Phi(x_1, x_2, \ldots x_N) &= \sum_k^{(G)} \mathbb{O}_k \Phi(x_1, x_2, \ldots x_N) = \\ &= \sum_k \Phi(k; x_1, x_2, \ldots x_N), \end{aligned} \tag{28}$$

which are eigenfunctions to the total translations $\mathfrak{T}_\nu$. Because of the general relations

$$\mathbb{O}_k^\dagger \mathbb{O}_l = 0, \qquad \mathbb{O}_k^\dagger \mathcal{H}\, \mathbb{O}_l = 0 \qquad (k \neq l), \tag{29}$$

these components are orthogonal and non-interacting with respect to the total Hamiltonian H.

In the following, we can concentrate our interest to a study of the <u>simultaneous</u> eigenfunctions to H and $\mathfrak{T}_\nu$. From the Schrödinger equation $H\Psi = E\Psi$ follows that $\mathcal{H}(\mathfrak{T}_\nu \Psi) = E(\mathfrak{T}_\nu \Psi)$ and, for a non-degenerate energy level, it is then evident that $\mathfrak{T}_\nu \Psi = \text{const.}\ \Psi$, i.e. $\Psi$ is also an eigenfunction to $\mathfrak{T}_\nu$. For a degenerate level, we consider instead the resolution of an arbitrary eigenfunction into Bloch-components according to (28), and it follows directly that each non-vanishing component is a simultaneous eigenfunction to H and $\mathfrak{T}_\nu$. Since $\mathfrak{T}_\nu$ is symmetric in all coordinates, the antisymmetry properties of the wave function will not be influenced by the projection (27).

In the Hartree-Fock approximation, we will now require that the total wave function represented by the single Slater determinant (2) should be an exact eigenfunction to the total translations $\mathfrak{T}_\nu$ ($\nu = 1, 2, 3$). This is simply

accomplished by choosing the one-electron functions as eigenfunctions $\psi(\mathbf{k}_i, \mathbf{r}_i)$ to the one-electron translations $T_\nu$, and one obtains

$$\mathfrak{k} = (\mathbf{k}_1 + \mathbf{k}_2 + \cdots + \mathbf{k}_N)_G \, , \tag{30}$$

where the index G means that one should take the reduced wave vector within the ground domain. The question is now whether such a choice <u>always</u> can be made, i.e. whether it follows from the requirement that the determinant (2) should be an eigenfunction to the total translations $\mathcal{T}_\nu$ that, except for an arbitrary unitary transformation, it is necessary that the basic spin-orbitals $\psi_1, \psi_2, \ldots \psi_N$ are Bloch functions satisfying the relation (16). A careful analysis of the problem shows that this is actually the case.

It seems rather natural to assume that the requirement that the basic spin-orbitals are Bloch functions also should be <u>self-consistent</u> in the sense of the Hartree-Fock scheme. From (4) and (16), it follows that

$$\rho(x_1 + a_\nu, x_2 + a_\nu) = \rho(x_1, x_2) \, , \tag{31}$$

where $(x + a_\nu)$ denotes the electronic coordinate $(\mathbf{r} + a_\nu, \zeta)$, and this relation implies that the electronic density has the periodicity of the lattice. Equation (31) is easily derived from the condition that the total wave function should be an eigenfunction to the total translations and is valid for the first--order density matrix in general. The density matrix $\rho$ is the crucial quantity in the effective Hamiltonian (3) and by means of (31), one can now prove the relation

$$T_\nu \mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{eff}} T_\nu \tag{32}$$

The first terms in $H_{\text{eff}}$ are easily handled, and only the exchange potential with its non-local character requires a more careful treatment. However, if $f(x_1)$ is an arbitrary function of $x_1$, one obtains

$$T_\nu(1)\int dx_2 \frac{\rho(x_2,x_1)\,P_{12}}{r_{12}} f(x_1) =$$

$$= \int dx_2 \frac{\rho(x_2, x_1+a_\nu)\, f(x_2)}{|r_1+a_\nu - r_2|} = \int dx_2 \frac{\rho(x_2+a_\nu, x_1+a_\nu)\, f(x_2+a_\nu)}{|r_1 - r_2|} \tag{33}$$

$$= \int dx_2 \frac{\rho(x_2,x_1)\,P_{12}}{r_{12}} T_\nu(1)\, f(x_1) ,$$

which proves that also the exchange term commutes with the primitive translations. Hence, the entire effective Hamiltonian $H_{eff}$ commutes with $T_1$, $T_2$, $T_3$, and the solutions to the eigenvalue problem (1) may then be chosen as simultaneous eigenfunctions to all these operators. For a crystal, the basic requirement that the Hartree-Fock functions $\psi_1, \psi_2, \dots \psi_N$ should be Bloch functions is thus self-consistent.

Each one of the $G^3$ points in the $\mathfrak{k}$ -space defined by (14) is independent in the sense that the associated Bloch functions are not only orthogonal but also non-interacting with respect to the effective Hamiltonian $H_{eff}$, as soon as $\rho$ satisfies (31). In forming $\rho$ according to (4), one should sum over all occupied spin-orbitals which are then associated with a certain distribution of points in $\mathfrak{k}$ -space. The boundary of these occupied points defines the Fermi-surface associated with the system and state under consideration.

Crystal Symmetry in General. - The translational symmetry has here been treated by a simple projection operator technique [17], which requires only the knowledge of the translational eigenvalues following from the Born- v. Kármán boundary condition (13), whereas no group theoretical information about the system is needed. It is evident, however, that a still richer understanding of this problem can be obtained by utilizing group theory to a full extent [20].

20) F. Seitz, Ann. Math. 37, 17 (1936); L.P. Bouckaert, R. Schmoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936); C. Herring, Phys. Rev. 52, 361, 365 (1937); and others.

In addition to the translational symmetry, there are also other symmetry properties of the different crystallographic point groups which may be used for dividing the various symmetry functions into non-combining classes [21]. Even in this connection, the use of projection operator technique has proven to be simple and forceful [22].

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21) H.A. Bethe, Ann. Physik 3, 133 (1929); Bouckaert et. al., Phys. Rev. 50, 58 (1936); F. Seitz, Phys. Rev. 47, 400 (1935); Z. Krist. 94, 100 (1936); C. Herring, J. Franklin Inst. 233, 525 (1942); J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954); and others.

22) M.A. Melvin, Revs. Modern Phys. 28, 18 (1956); H. McIntosh, Technical Note 21, Uppsala Quantum Chemistry Group 1958; J. Mol. Spectroscopy 5, 269 (1960).

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### (c) Calculations of Band Structures

The main problem in the one-electron theory of crystals is the solution of the Hartree-Fock equations (1), which gives the spin-orbital energies $\epsilon = \epsilon(k)$ as a multi-valued function over the first Brillouin zone or over the ground domain in the space of the reduced wave vector $k$, and hence also the band structure. Since this is one of the key problems in the current solid-state theory, it is frequently reviewed, and for a detailed discussion of the progress in this field, we will refer to a series of survey articles [23]. The recent papers by Herman [24] and by Pincherle [25] are particularly complete, and there is no reason to repeat the material contained in these articles. Here only a few additional remarks will be made, certain problems will be discussed from slightly different points of view, and some recently published papers will be listed and commented upon.

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23) G.V. Raynor, Repts. Prog. Phys. 15, 173 (1952); J.R. Reitz, Solid State Physics 1, 1 (Academic Press, New York 1955); P.O. Löwdin, Advances in Physics 5, 1 (1956); J.C. Slater, Encyclopedia of Physics 19, 1 (Springer, Berlin 1956).

24) F. Herman, Revs. Modern Phys. 30, 102 (1958).

25) L. Pincherle, Repts. Prog. Phys. 23, 355 (1960).

The essential difficulty in the one-electron theory of crystals seems to be connected with the fact that the wave functions have atomic nature within the ion cores, whereas they behave as free waves in the regions between the atoms, and these properties are apparently hard to combine - at least practically.

In Ritz's method [9], one expands the wave function $\psi_k$ in terms of a complete set $\{f_l\}$ :

$$\psi_k = \sum_l f_l c_l , \tag{34}$$

where the problem is to determine the coefficients. It is convenient to introduce the energy matrix $\mathbf{H}$ with respect to the basis and the associated metric matrix $\mathbf{\Delta}$ having the elements:

$$\mathcal{H}_{mn} = \langle f_m | \mathcal{H}_{eff} | f_n \rangle , \qquad \Delta_{mn} = \langle f_m | f_n \rangle , \tag{35}$$

and the Schrödinger equation $H_{eff}\psi_k(1) = \epsilon_k \psi_k(1)$ is then equivalent with the following system of linear equations:

$$\sum_m (\mathcal{H}_{mn} - \epsilon \Delta_{mn}) c_m = 0 , \tag{36}$$

with the secular equation $\det (\mathcal{H}_{mn} - \epsilon \Delta_{mn}) = 0$ .

The matrix problem (36) can be essentially simplified if one utilizes the existence of the translational symmetry. Since the wave functions $\psi_k$ should be Bloch functions $\psi(\mathbf{k}, \mathbf{x})$, they are invariant against the corresponding Bloch projection (17), so that $O_k \psi_k = \psi_k$. By applying the operator $O_k$ to both sides of (34), one obtains

$$\psi_k = \sum_l (O_k f_l) c_l , \tag{37}$$

which means that each Bloch function may be expanded in the associated Bloch

projection of any complete set. The functions within the subset $\{ O_{\mathbf{k}} f_l \}$ are usually not linearly independent, and an essential problem is to eliminate the redundancies in expansion (37) and replace it with a rapidly convergent series. This can, for instance, be done by an orthonormalization procedure [26), but

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26) P.O. Löwdin, Adv. Chem. Phys. 2, 207 (Interscience, New York 1959), p. 288 f.

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even other possibilities exist. Here we note that, by replacing the complete set $\{ f_l \}$, by the $G^3$ subsets

$$\{ O_{\mathbf{k}} f_l \} \tag{38}$$

which are mutually orthogonal and non-interacting with respect to $H_{eff}$, one obtains automatically a splitting of the secular equation (36) into $G^3$ independent parts, each one corresponding to a specific point $\mathbf{k}$ in the space of the reduced wave vector. This is an essential simplification of the problem which it is always possible to carry out.

The main problem in the application of the expansion method to crystal theory seems to be the choice of the subsets $\{ O_{\mathbf{k}} f_l \}$ so that the convergency of the series (37) becomes as fast as possible [27)]. If the basic set $\{ f_l \}$ is chosen to consist of plane waves [18)] (PW), the convergency will usually be very slow, since many waves will be needed to describe the inner atomic properties of the constituents of the crystal. In the method of orthogonalized plane waves (OPW) devised by Herring [28)], the convergency is essentially

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27) We note that, since the subsets are entirely independent, one may use different complete sets $\{ f_l \}$, $\{ f_l' \}$, $\{ f_l'' \}$, .... or various adjustable parameters for different values of $\mathbf{k}$ which may often improve the convergency.

28) C. Herring, Phys. Rev. 57, 1169 (1940).

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improved by choosing a basis which consists of the Bloch projections of the inner-core atomic orbitals and the plane waves orthogonalized towards these

functions. In applying this method to a practical problem, one has to remember that the inner-core Bloch functions and the OPW's are usually interacting with respect to the effective Hamiltonian, i.e. the corresponding matrix elements are not necessarily vanishing even if they may be small [29]. As a practical tool, the method has been very forceful, and many important applications have been carried out; see Herman [24] and Pincherle [25].

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29) For critical studies of the method, see J. Callaway, Phys. Rev. 97, 933 (1955); V. Heine, Proc. Roy. Soc. (London) A240, 340, 354, 361 (1957); T. O. Woodruff, Solid State Physics 4, 367 (Academic Press, New York 1957).

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From studies of the Knight shift, it has recently been observed that an OPW-calculation which gives good results e.g. with respect to cohesive and elastic properties or the band structure may not describe the regions around the nuclei very well, and particularly for the beryllium metal there seems to be a large discrepancy between theory and experiment in this respect [30]. Of course, this is a consequence of the fact that the basic sets

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30) L. Jansen (private communication).

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are truncated in all applications, and that the "remainder problem" has not been investigated. If the inner-core Bloch functions chosen are not particularly adapted for describing the nuclear region, one has certainly to introduce a much larger number of OPW's than used in studying other properties of less local type.

A modification of the OPW-method has recently been suggested by Phillips and Kleinman [31] who start out from symmetrized combinations of plane waves instead of single waves; the method seems to work very well in the applications [32]. In the OPW-approach, it may sometimes also be

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31) J.C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

32) L. Kleinman and J.C. Phillips, Phys. Rev. 116, 880 (1959), diamond; 117, 460 (1960), BN; 118, 1153 (1960), Si.

worthwhile to use flexible auxiliary functions instead of the fixed inner-core orbitals to speed up the convergency [33].

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33) E. Brown and J.A. Krumhansl, Phys. Rev. 109, 31 (1958).

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In Slater's [34] method of augmented plane waves (APW), the space

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34) J.C. Slater, Phys. Rev. 51, 846 (1937); 92, 603 (1953); M.M. Saffren and J.C. Slater, Phys. Rev. 92, 1126 (1953); R.S. Leigh, Proc. Phys. Soc. (London) A69, 388 (1956).

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around each atomic nucleus is divided into an inner sphere approximately corresponding to the ion core and an outer region, where plane waves are conveniently used. The Schrödinger equation (1) is solved in both regions with solutions of different character which are then joined smoothly on the boundary spheres. The method shows very good convergency properties, and a series of important applications to the problem of the band structure of various crystal has been carried out; see Herman [24] and Pincherle [25].

It has previously been mentioned here that the tight-binding method introduced by Bloch [12] in crystal theory in its most refined form corresponds to the ASP-MO-LCAO-SCF-method in molecular theory [11, 13]. In the first applications, the method did not give any good results, since one neglected the overlap integrals between atomic orbitals on neighboring atoms. It turned later out that these overlap integrals were key quantities of essential importance for the entire theory. The non-orthogonality problem may be handled by starting from orthonormalized atomic orbitals [35, 36] or from Wannier functions [37]. A

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35) R. Landshoff, Z. Physik 102, 201 (1936).

36) P.O. Löwdin, Arkiv Mat., Fys., Astr. 35A, No. 9 (1947); "A theoretical Investigation Into some Properties of Ionic Crystals" (Thesis, Almqvist and Wiksell, Upsala 1948); J. Chem. Phys. 18, 365 (1950).

37) G.H. Wannier, Phys. Rev. 52, 191 (1937).

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more complete discussion of the tight-binding approach will be given in Sec. 4.

The Wannier functions [37] are the Fourier transforms of the Bloch functions, and they form a complete set of mutually orthogonal functions localized around the lattice points and connected by translational symmetry. They form an excellent basis for investigating crystal properties, and one has tried to find direct methods for determining them; for references, see Herman [24] and Pincherle [25]. Some important new results concerning the localization of the Wannier functions have recently been obtained [38]. Functions intermediate between Bloch waves and Wannier functions have also been introduced [39].

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38) W. Kohn and S. Michaelson, Proc. Phys. Soc. (London) 72, 301 (1958); W. Kohn, Phys. Rev. 115, 809 (1959).

39) E.C. McIrvine and A.W. Overhauser, Phys. Rev. 115, 1531 (1959).

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In the Hartree-Fock scheme, the total wave function (2) and the density matrix (4) are invariant with respect to unitary transformations of the basic spin-orbitals $\psi_1, \psi_2, \ldots, \psi_N$. It was pointed out by Lennard-Jones [40]

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40) J. Lennard-Jones, Proc. Roy. Soc. (London) A198, 1, 14 (1949), and a series of papers by Lennard-Jones, Hall, and Pople during the years 1950-52; for detailed references, see G.G. Hall, Proc. Roy. Soc. (London) 213, 113 (1952).

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that, instead of molecular orbitals and Bloch functions, it may sometimes be convenient to introduce a localized set of orbitals which are all equivalent to the atoms of the system. This equivalent orbital method has now been applied by Hall [41] for investigating the electronic structure of certain crystals of diamond type. The problem of the solution of the Hartree-Fock equations (1) in terms of localized orbitals has recently been studied also by Adams [42].

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41) G.G. Hall, Phil. Mag. (7) 43, 338 (1952), diamond; Phil. Mag. (8) 3, 429 (1958), Si, Ge, and diamond.

42) W.H. Adams, J. Chem. Phys. 34, 89 (1961).

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Let us now return to the Bloch functions $\psi(\mathbf{k}, \mathbf{r})$. As previously shown, these functions are associated with $G^3$ points in the space of the reduced wave vector $\mathbf{k}$, and they are orthogonal and non-interacting with respect to the effective Hamiltonian. Since the number of independent points is so enormously large, one has to treat only a selection of k-values which are usually chosen to correspond to symmetry points in the reciprocal lattice [43]. In each such point, one tries to find the Bloch function, the energy $\epsilon = \epsilon(\mathbf{k})$ and its first and second derivatives, and an essential problem is then the interpolation to intermediate $\mathbf{k}$-values. This problem has been attacked by a simplified LCAO-method [44] and by a method based on the use of a pseudo--potential [45]; in all events, a great deal of care is necessary to get reliable results.

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43) F.C. von der Lage and H.A. Bethe, Phys. Rev. 65, 255 (1944); 71, 612 (1947).

44) J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954); M. Miasek, Phys. Rev. 108, 92 (1957).

45) J.C. Phillips, Phys. Rev. 112, 685 (1958).

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It follows from the condition (16) that each Bloch function may be written in the form

$$\psi(\mathbf{k}, \mathbf{r}) = e^{2\pi i \mathbf{k}\cdot\mathbf{r}} u(\mathbf{k}, \mathbf{r}) , \qquad (39)$$

where u is a function with the periodicity of the lattice, so that $u(\mathbf{k}, \mathbf{r}+\mathbf{a}_\nu) = u(\mathbf{k}, \mathbf{r})$. Instead of determining the Bloch function within the entire micro-crystal, it is now sufficient to evaluate $u(\mathbf{k}, \mathbf{r})$ within a unit cell or an equivalent region. It is convenient to introduce the "cellular polyhedron" consisting of all non-equivalent points in the ordinary lattice having the smallest value of $|\mathbf{r}|^2$; its boundaries are defined by the relations

$$\mathbf{r}' - \mathbf{r} = \mathbf{m} , \qquad |\mathbf{r}|^2 = |\mathbf{r}'|^2 , \qquad (40)$$

analogous to (23), and the "cellular polyhedron" in the ordinary lattice corresponds

apparently to the first Brillouin zone in the reciprocal lattice. It follows from (40) that the boundaries are the planes bisecting perpendicularly the lines between the origin and the nearest neighbours among its equivalent points.

In the cellular method developed by Wigner and Seitz [46], one tries to determine the function $u(\mathbf{k}, \mathbf{r})$ by numerical integration in analogy with Hartree's treatment of atoms [6]. Wigner and Seitz assumed that it was possible to approximate $u(\mathbf{k}, \mathbf{r})$ by an s-function independent of $\mathbf{k}$ but later the importance of the higher spherical harmonics was emphasized [47],

46) E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

47) J.C. Slater, Phys. Rev. 45, 794 (1934); Revs. Modern Phys. 6, 209 (1934).

and u should actually be expanded in the form:

$$u(\mathbf{k}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} R_{lm}(\mathbf{k}, \mathbf{r}) \, Y_{lm}(\vartheta, \varphi) \quad , \tag{41}$$

where the radial functions should, in principle, be determined by numerical integration. The difficulty of the method is to get the periodicity condition $u(\mathbf{k}, \mathbf{r}+\mathbf{a}_\nu) = u(\mathbf{k}, \mathbf{r})$ satisfied on the boundary planes of the cellular polyhedron or at least in a selected set of symmetry points [48], when the series

48) W. Shockley, Phys. Rev. 52, 866 (1937); F.C. von der Lage and H.A. Bethe, Phys. Rev. 71, 612 (1947); W. Kohn, Phys. Rev. 87, 472 (1952).

(41) is truncated. It should be observed that, if the resulting function $\exp(2\pi i \mathbf{k}\cdot\mathbf{r})\, u(\mathbf{k}, \mathbf{r})$ is not a true Bloch function, it can always be resolved into Bloch components by using the projection technique and formula (20). The cellular method has been applied to the problem of band structure for a series of crystals of various types; for references, see Herman [24] and Pincherle [25].

The cellular method was actually deviced for a study of the cohesive

properties of the alkali metals [49], but in this field it has to a certain extent been replaced by the semi-empirical quantum defect method introduced by Kuhn and Van Vleck [50] and developed by Brooks [51]; for a survey, see Ham [52].

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49) See e.g. the survey by E. Wigner, Proc. Int. Conf. Theor. Phys. Japan, 649 (Tokyo 1954).

50) T.S. Kuhn and J.H. van Vleck, Phys. Rev. 79, 382 (1950); T.S. Kuhn, Phys. Rev. 79, 515 (1950); Quart. Appl. Math. 9, 1 (1951); Proc. Int. Conf. Theor. Phys. Japan, 640 (Tokyo 1954).

51) H. Brooks, Phys. Rev. 91, 1027 (1953).

52) F.S. Ham, Solid-State Physics, 1, 127 (Academic Press, New York 1955).

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It is a characteristic feature of most of the present calculations within the one-electron scheme for crystals that the potential in the effective Hamiltonian is assumed to be a crystal potential of the periodicity of the lattice which is derived from semi-empirical arguments or theoretical considerations. In the Hartree-Fock scheme, the potential in (3) contains a conventionally periodic part and an exchange term of a non-local character. The evaluation of the effective Hamiltonian requires the knowledge of all functions $\psi(\mathbf{k}, \mathbf{r})$ with k-values within the Fermi surface, which means that a good solution to the interpolation problem is usually necessary. It is apparently very cumbersome to carry through a single Hartree-Fock cycle (5), not to speak of a series of iterations of this cycle, and it is hence extremely important that one is able to start from a good estimate of the crystal potential including exchange. Of course, one hopes that the band structure and other physical results should not be too dependent on the specific choice of potential, but the work by Howarth [53] on

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53) D.J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953); Phys. Rev. 99, 469 (1955).

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copper shows that this is not always the case. It seems hence important to try to reach the goal of self-consistency for a real cyrstal, but we note that, even if one obtains the exact Hartree-Fock functions, the corresponding Slater determinant (2) is still rather far from the true many-electron function.

The one-electron scheme has up till now been used to determine the spin-orbital energies $\epsilon = \epsilon(\mathbf{k})$ and the corresponding band structure for a large number of crystals. It has been of essential importance as the underlying theoretical tool for interpreting experiments [54], and it is of great

[54] B. Lax, Revs. Modern Phys. 30, 122 (1958).

value for understanding the electric, magnetic, optical, thermal, and elastic properties of solids. At the same time, the present band theory is certainly not sufficient to explain such phenomena as refer to the solid as a whole as, for instance, the cohesive properties, the relative stability of various lattice types, the criterion for ferromagnetism, etc. The background for this failure will now be discussed.

### (d) Shortcomings of Band Theory; Correlation Error

The one-particle model is based on the idea that the particles move independently of each other. This happens, for instance, if the total Hamiltonian $H_{op}$ is separable in the form $H = \sum_i H_i$, and the total wave function is then a product of one-particle functions or spin-orbitals. In reality, the total Hamiltonian (7) has the form

$$\mathcal{H}_{op} = \mathcal{H}_{(0)} + \sum_{i=1}^{N} \mathcal{H}_i + \sum_{i<j} \mathcal{H}_{ij} \, , \qquad (42)$$

where $H_{ij}$ is a two-electron operator: $H_{ij} = e^2/r_{ij}$. Because of this Coulomb repulsion, two electrons try always to avoid each other to keep the energy as low as possible, and this leads to a certain "correlation" between their movements. Since the two electrons have actually to perform a more complicated motion than in the independent-particle model, there will be an increase in the kinetic energy which is compensated by a still larger decrease in the Coulomb energy; the balance is regulated by the virial theorem $\langle T \rangle = -\frac{1}{2}\langle V \rangle$. One can say that each electron is surrounded by a "Coulomb hole" with respect to all other electrons, and the omission of this phenomenon leads to the correlation error characteristic for the independent-particle-model.

The correlation effect is most easily discussed by means of the second--order density matrix [55]:

[55] P.O. Löwdin, Phys. Rev. 97, 1474 (1955); R. McWeeny, Proc. Roy. Soc. (London) A232, 114 (1955); see also K. Husimi, Proc. Phys.-Math. Soc. Japan 22, 264 (1940).

$$\Gamma(x_1 x_2 | x_1' x_2') = \sum_{i<j} \int \Psi(x_i x_j \dots x_1 \dots x_2 \dots)\, \Psi^*(x_i x_j \dots x_1' \dots x_2' \dots)\, dx_3 dx_4 \dots dx_N, \tag{43}$$

where one should sum over the N(N-1)/2 possibilities of exchanging the coordinates $x_1$ and $x_2$ - as well as $x_1'$ and $x_2'$ - with the coordinates $x_i$ and $x_j$, respectively, in the total wave function $\Psi$. The diagonal element $\Gamma(x_1 x_2 | x_1 x_2)$ gives the probability density to find an electron pair in the points $x_1 = (r_1, \zeta_1)$ and $x_2 = (r_2, \zeta_2)$ in configuration space. The coulomb energy of the electron is given by the expression

$$e^2 \iint \frac{\Gamma(x_1 x_2 | x_1 x_2)}{r_{12}}\, dx_1 dx_2, \tag{44}$$

and the existence of a "Coulomb hole" means that the quantity $\Gamma(x_1 x_2 | x_1 x_2)$ should be small when $r_{12} = |r_1 - r_2|$ tends to zero.

A study of the second-order density matrix shows that, if the total wave function is approximated by a Hartree-product, there will be no correlation whatsoever between the electrons 1 and 2. The situation is changed by the anti-symmetrization and, if the total wave function is approximated by a single Slater determinant, the density matrix $\Gamma(x_1 x_2 | x_1' x_2')$ will become antisymmetric in each set of its indices. This implies that $\Gamma(x_1 x_2 | x_1 x_2)$ will vanish of at least second order for $x_1 = x_2$, i.e. $r_{12} = 0$ and $\zeta_1 = \zeta_2$. This is the "Fermi hole" for electrons with parallel spins [56] and, since this

[56] E. Wigner, and F. Seitz, Phys. Rev. 43, 804 (1933); J.C. Slater, Phys. Rev. 81, 385 (1951); V.W. Maslen, Proc. Phys. Soc. (London) A69, 734 (1956).

hole to a certain extent replaces the Coulomb hole, the main part of the correlation error for electrons with parallel spins is removed. In the Hartree--Fock scheme, the essential correlation error is hence associated with electrons having antiparallel spins.

In order to get a measure of the order of magnitude of the correlation error in the Hartree-Fock scheme, it is convenient to introduce the concept of "correlation energy"[57], as the difference:

$$E_{corr} = E_{exact} - E_{HF} \tag{45}$$

57) E. Wigner, Phys. Rev. <u>46</u>, 1002 (1934); Trans. Faraday Soc. <u>34</u>, 678 (1938); F. Seitz, "Modern Theory of Solids" (McGraw Hill, New York 1940) p. 698 f; J.C. Slater, Revs. Modern Phys. <u>25</u>, 199 (1953); E.P. Wohlfarth, Revs. Modern Phys. <u>25</u>, 211 (1953); D. Pines, "Solid State Physics" <u>1</u>, 368 (Academic Press, New York 1955); P.O. Löwdin, Adv. Chem. Phys. <u>2</u>, 207 (Interscience, New York 1959).

where $E_{exact}$ is the true eigenvalue of the Hamiltonian for the state under consideration and $E_{HF}$ the corresponding Hartree-Fock energy. We note that the correlation energy is not a physical quantity but a measure of the error in a certain approximation. Two aspects of the correlation problem will be of particular importance:

a) the correlation error for the equilibrium state ($R = R_o$)

b) the correlation error for separated atoms ($R \approx \infty$)

where $R$ is a parameter indicating the internuclear distances.

Let us start the discussion by reviewing some data from atomic and molecular theory[26]. For the series of helium-like ions ($H^-$, He, $Li^+$, ..... $C^{4+}$) in their $(1s)^2$ ground state, the correlation energy is remarkably constant[58, 59] and varies between -1.1 and -1.2 eV, whereas for the ground

58) H. Shull and P.O. Löwdin, J. Chem. Phys. <u>24</u>, 1035 (1956); <u>30</u>, 617 (1959).

59) A. Fröman, Phys. Rev. <u>112</u>, 870 (1958).

state of the Ne-like ions [59], it lies around -11 eV. For atoms and ions without closed shells [60], the correlation energy varies approximately linearly with

60) J. Linderberg and H. Shull, J. Mol. Spectroscopy 5, 1 (1960).

the atomic number $Z$. For the hydrogen molecule, the correlation energy is -1.06 eV, and we note that, according to the virial theorem, this quantity consists of two parts, namely the correlation error in the kinetic energy and the corresponding error in the potential energy:

$$T_{corr} = +1.06 \text{ eV} , \qquad V_{corr} = -2.12 \text{ eV}. \tag{46}$$

Since 1 eV = 23.07 kcal/mole, these quantities are large from the chemical point of view.

The problem of the error in the molecular-orbital theory for separated atoms was first investigated in a classical paper by Slater [61], where he studied the connection between the molecular-orbital approach and the valence-bond

61) J.C. Slater, Phys. Rev. 35, 509 (1930).

method by using the hydrogen molecule as an example. If $a$ and $b$ are the atomic orbitals, the total wave function in the MO-LCAO method takes the form

$$\underline{\Psi} = (a_1 + b_1)(a_2 + b_2)(\alpha_1\beta_2 - \alpha_2\beta_1) , \tag{47}$$

which implies that, for separated atoms, there is a fifty per cent chance that the molecule will dissociate into the ions $H^-$ and $H^+$, and an equal chance that it will dissociate into two H atoms. The energy of the former is considerably higher than the energy of the latter, and the resulting error is of the order 8 eV.

The weakness of the molecular-orbital theory and of the band theory of solids is apparently that the total wave function is such that it does not prevent electrons of different spins to accumulate on the same atom and give rise to negative and positive ions [62] with higher energy than the ordinary dissociation

62) J.H. Van Vleck and A. Sherman, Revs. Modern Phys. 7, 167 (1935).

products. In nature, the strong Coulomb repulsion between the electrons prevents the formation of negative ions with too many electrons, but apparently this correlation effect has been neglected in the Hartree-Fock scheme. The error is so large that one can speak of a complete breakdown of the independent-particle model and the molecular-orbital theory for separated atoms [63].

63) C.A. Coulson, and I. Fischer, Phil. Mag. 40, 386 (1949).

Slater [64] has emphasized that the wrong asymptotic behaviour of the singlet energy curve for $R = \infty$ has a very serious consequence with respect to the study of magnetic properties. In a state where the electrons have parallel spins, the Pauli-principle will prevent the formation of negative ions, and the energy will approach the correct value for $R = 0$. The general shape of the energy curves is indicated in Fig. 1. Since the $\uparrow\downarrow$ -curve has a wrong asymptotic behaviour for $R = \infty$, there will always be an artificial crossing point with the $\uparrow\uparrow$ -curve, which may lead to wrong conclusions about the general magnetic properties of the system. This may cause difficulties in a theory of ferromagnetism based essentially on band theory [65]. Apparently the difficulty comes from the fact that the Hartree-Fock scheme treats electrons with parallel spins fairly well, whereas the study of electrons having antiparallel spins shows a large correlation error [66], which has to be removed.

64) J.C. Slater, Phys. Rev. 82, 538 (1951); Revs. Modern Phys. 25, 199 (1953); Encyclopedia of Physics 19, 1 (Springer, Berlin 1956).

65) For a review, see e.g. E.C. Stoner, Repts. Prog. Phys. 11, 43 (1948); J. phys. radium 12, 372 (1951); E.P. Wohlfarth, Revs. Modern Phys. 25, 211 (1953).

66) D. Pines, Proc. 10th Solvay Conference, 9 (1954).

The correlation error does not always show up in a calculation, which depends on the fact that we are often interested in energy differences, and it may happen that the correlation errors associated with each term to a large

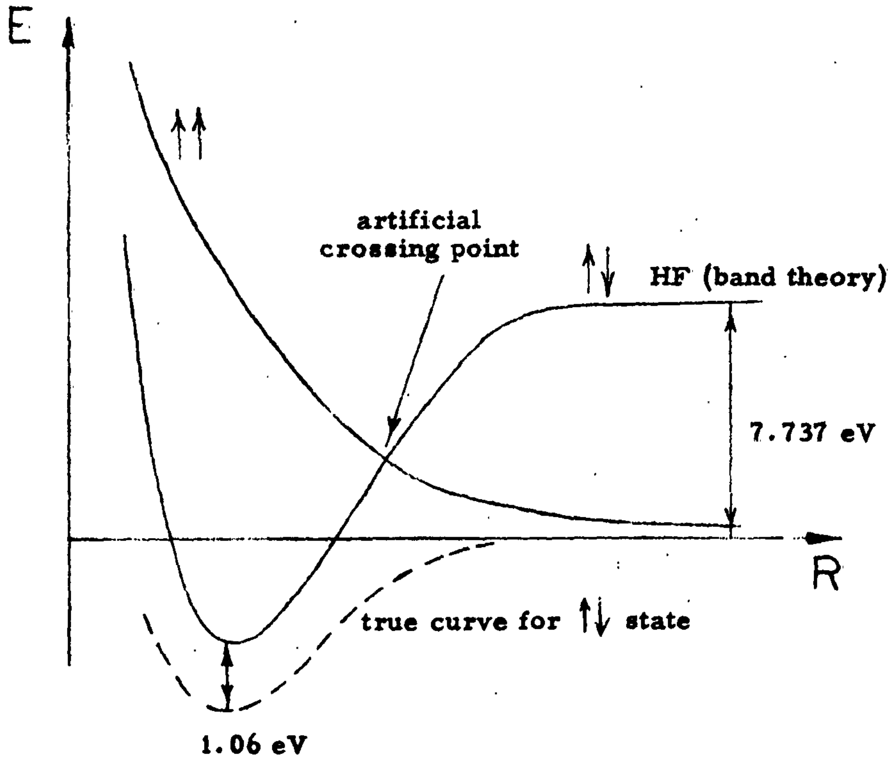


Fig. 1. Energy curves for state of lowest and highest multiplicities as functions of internuclear distance R ; numerical data refer to $H_2$- molecule.

extent cancel. This happens, for instance, in studying the cohesive energy of an ionic crystal of the type of the alkali halides, since the electronic structure of the constituents and of the free ions are similar, and the correlation energy of the crystal is then approximately equal to the correlation energy of the free ions.

On the other hand, there is certainly no such cancellation in an investigation of the cohesive energy of the alkali metals. The correlation error for this case has been studied in great detail by Wigner [57, 48], who derived the correlation energy formula

$$-0.288 \frac{e^2}{r_s + 5.1} , \tag{46}$$

where all quantities are expressed in atomic units. For the alkali metals Li, Na, K, one obtains the following values for the correlation energy per doubly filled orbital, namely -1.89, -1.73, -1.58 eV, respectively.

According to Wigner, the correlation energy should essentially be a function of the electron density. Of particular importance is Wigner's study of the low density limit which is based on the plasma model, in which the electrons in a crystal are approximated by an electron gas moving in a "uniform positive background". For sufficiently low density, the electrons will form a body-centered cubic lattice with interesting properties [67].

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67) W.J. Carr Jr., Phys. Rev. 112, 1437 (1961).

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The plasma model has later been strictly treated by Bohm and Pines [68] using field-theoretical methods. According to classical discharge theory, such

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68) For a survey, see D. Pines, Phys. Rev. 92, 626 (1953) and reference 66.

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a plasma shows a collective oscillatory behaviour with the fundamental frequency $\omega_p = (4\pi n_0 e^2/m)^{\frac{1}{2}}$ , where $n_0$ is the average electron density. The field-theoretical study of the electronic correlation showed a long-range effect corresponding to the plasma oscillations and a short-range effect giving raise to an efficient electronic screening, which later has become of large importance in the so-called "dielectric approximation".

Since in the simple plasma model there are no discrete nuclei, such aspects of the correlation problem as are concerned with the atomic constituents of a crystal will not be treated whatsoever. The problem of the asymptotic behaviour of the energy for separated atoms so strongly emphasized by Slater [64] cannot be treated at all within the framework of this model. In the atomic approach, the correlation energy is certainly not a function of the electronic density only and, as an example, we would consider the series of helium-like ions which all have the same correlation energy, but which goes from the extremely extended $H^-$ ion to the highly concentrated positive ions, like $C^{4+}$. Even if the simple plasma model has given very interesting and important results concerning the behaviour of the mobile electrons in metals, it has so far not given the ultimate answer to the problem of the correlation error in the band theory of ordinary crystals with discrete atomic nuclei. This question will be further discussed below.

## 3. VALENCE BOND METHOD

### (a) Covalent Bond; Valence Bond Functions

Crystal physics can be approached from an entirely different point of view than band theory. In connection with e.g. cohesive properties, it seems natural to start from the chemists' ideas of bonding between atoms to describe the binding of the constituents of a crystal, and this leads to the valence bond method. According to Lewis, each covalent bond is associated with an electron pair which causes the binding, but the real nature of the bond was not revealed until the establishment of modern quantum mechanics. In connection with the problem of the helium atom, Heisenberg [69] had discovered the exchange phenomenon and the identity principle which says that it is physically impossible to distinguish between the individual electrons. In modern terminology, it means that the permutation operator $P_{12}$ is a constant of motion, so that $P_{12}H = HP_{12}$. In investigating the hydrogen molecule, Heitler and London [70] found that the bonding of the atoms depended on this exchange effect and had hence essentially a quantum mechanical character.

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69) W. Heisenberg, Z. Physik <u>38</u>, 411 (1926); <u>39</u>, 499 (1926).

70) W. Heitler and F. London, Z. Physik <u>44</u>, 466 (1927).

Let $\Phi = \Phi(r_1, r_2)$ be a space function which describes the physical situation of an electron pair. By means of the identity

$$1 = \frac{1}{2}(1 + P_{12}) + \frac{1}{2}(1 - P_{12}) , \tag{47}$$

where each term in the right-hand member is a projection operator, one can resolve this function into its symmetric and antisymmetric components with respect to $P_{12}$, which are orthogonal and non-interacting with respect to $H$. The symmetric space component is associated with the singlet state, and the antisymmetric space component with the triplet state and, for the corresponding energies, one obtains

$${}^1E = \frac{\langle \Phi | \mathcal{H} + \mathcal{H}P | \Phi \rangle}{\langle \Phi | 1 + P | \Phi \rangle} , \tag{48}$$

$${}^3E = \frac{\langle \Phi | \mathcal{H} - \mathcal{H}P | \Phi \rangle}{\langle \Phi | 1 - P | \Phi \rangle} , \tag{49}$$

which quantities should be compared with the expectation value $\langle \Phi | \mathcal{H} | \Phi \rangle / \langle \Phi | \Phi \rangle$, which always lies between them. In this connection, it is convenient to introduce the <u>exchange integral</u>:

$$J = \frac{1}{2}({}^1E - {}^3E) , \tag{50}$$

which may then be used as a criterion for the spin alinement. If $J > 0$ one has ${}^1E > {}^3E$ and parallel spins in the ground state, whereas, for $J > 0$, one has ${}^1E < {}^3E$ and antiparallel spins in the ground state. According to this simple model, the exchange integral would then give the criterion for ferromagnetism versus antiferromagnetism, if the concept could be generalized to crystals. Substitution of (48) and (49) into (50) gives the expression:

$$J = \frac{\langle \Phi | \mathcal{H}P | \Phi \rangle - \langle \Phi | \mathcal{H} | \Phi \rangle \langle \Phi | P | \Phi \rangle}{\langle \Phi | \Phi \rangle^2 - \langle \Phi | P | \Phi \rangle^2} . \tag{51}$$

Originally, the valence bond theory was based on the one-electron approximation according to which one has $\Phi(1,2) = a(1)\,b(2)$ where $a$ and $b$ are two atomic orbitals (AO's) associated with the two constituents. The quantity $S_{ab} = \langle a|b\rangle$ is known as the "overlap integral" and plays an important role in the theory. We note that one cannot start out from two orthogonalized AO's, $\bar{a}$ and $\bar{b}$ since the singlet would then not show any bonding [71]; the exchange integral $J$ would further be positive, so that the triplet would be the ground state. The overlap problem is hence very essential.

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71) J.C. Slater, J. Chem. Phys. 19, 220 (1951).

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A careful analysis of the connection between the band theory or MO--method and the valence bond (VB) scheme was made by Slater [61], who used the $H_2$-molecule as a typical example. He showed that the VB-method including polar states, $a(1)\,a(2)$ and $b(1)\,b(2)$, would give the same result as the MO--method including configurational interaction between the bonding orbital $(a+b)$ and the anti-bonding orbital $(a-b)$. However, in their original and naive forms, the two approaches are certainly not equivalent. For the equilibrium state $(R = R_0)$, they lead to rather similar results, whereas for separated atoms $(R \approx \infty)$, the naive VB-method is superior to the naive MO-method, since the former gives a correct asymptotic behaviour of the singlet energy curve. In this respect, there is less correlation error in the naive valence bond method than in the ordinary band theory.

The total wave function for a valence bond singlet associated with an orbital pair $(a,b)$ may be written in the form $A a_1 b_2 (\alpha_1\beta_2 - \beta_1\alpha_2)$ where $A$ is the antisymmetrization operator. This construction is easily generalized [72,73]

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72) W. Heitler and G. Rumer, Göttinger Nachr. 1930, 277.

73) G. Rumer, Göttinger Nachr. 1932, 337.

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to a many-electron system having the orbital-pairs $(ab)$, $(cd)$, $(ef)$, ... etc., and the total valence-bond singlet is given by the expression

$$^1\Phi = \mathcal{A}\, a_1 b_2 c_3 d_4 e_5 f_6 \ldots (\alpha_1\beta_2 - \beta_1\alpha_2)(\alpha_3\beta_4 - \beta_3\alpha_4)(\alpha_5\beta_6 - \beta_5\alpha_6)\ldots, \tag{52}$$

where there is one spin singlet $(\alpha\beta - \beta\alpha)$ for each orbital pair. The collection of orbitals a, b, c, d, e, f, ... may, of course, be paired in many different ways, and each one gives rise to a valence bond singlet. The correct number of linearly independent valence bond singlets may be found by means of Rumer's non-crossing rule [73,74] for the valence bonds. There is a close parallelism between the quantum-mechanical wave function and the corresponding chemical formula for the compound, which has been further developed in the theory of chemical resonance [75].

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74) L. Pauling, J. Chem. Phys. 1, 280 (1933).

75) J.C. Slater, Phys. Rev. 37, 481 (1931); particularly p. 489, L. Pauling, J. Chem. Phys. 1, 280 (1933), and a series of papers in J. Chem. Phys. and J. Am. Chem. Soc.

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In the case when the overlap integrals between the orbitals a, b, c, d, ... are neglected, the expectation value of the total energy and its matrix elements with respect to the valence bond singlets are fairly easily evaluated [74]. However, this approach will not describe chemical bonding unless the overlap integrals are included, and it turns then out to be extremely cumbersome to calculate the elements of the energy matrix [76]. The best way to solve this problem systematically seems to be to resolve the valence bond singlets into spin-projections of Slater determinants [77]. The valence bond singlets are hence physically simple but, with respect to the energy, mathematically complicated.

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76) See e.g. J.C. Slater, Quarterly Progress Report of Solid-State and Molecular Theory Group, M.I.T., p. 3, October 15, 1953 (unpublished).

77) P.O. Löwdin, Technical Note 2, Uppsala Quantum Chemistry Group (1957); Coll. Int. Centre Nat. Rech. Sci. 82, 23, Paris 1958.

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If the overlap problem is difficult for a molecule, it becomes almost prohibitive for a crystal. It was pointed out by Slater [61] that the inclusion of the overlap integrals in the application of the VB-method to crystals would lead to divergency difficulties of such a severe type that one has later called it a "non-orthogonality catastrophe" [78]. Actually, each matrix element of

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78) D.R. Inglis, Phys. Rev. 46, 135 (1934).

the energy is of the form $\infty/\infty$ but, in the denominator and the numerator, there is a common infinite factor, and the remaining quotient is well-behaved. This problem is still not completely solved in all details, and we will comment more about it below.

Another problem in the VB-theory for treating crystals is that apparently the polar states are of fundamental importance, particularly in connection with conductivity phenomena. The basic theory shows many interesting aspects [79)] but is rather complicated in the applications. A simplification of this approach could be obtained, if one could, in principle, include all polar states, since one could then use orthogonalized atomic orbitals or Wannier functions as a basis [80)].

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79) S. Schubin, and S. Wonssowsky, Proc. Roy. Soc. 145, 159 (1934); Physik. Z. Sowjetunion 7, 292 (1935); 10, 348 (1936); S. Wonssowsky, Fortschritte der Physik 1, 239 (1954).

80) For a study of the molecular case, see R. McWeeny, Proc. Roy. Soc. (London) A223, 63, 306 (1954).

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Starting from the chemists' point of view, Pauling [81)] has developed a resonating-valence-bond theory of metals, which seems to be remarkably successful as a semi-empirical device. A valence-bond treatment based on the use of bond orbitals instead of atomic orbitals [82)] should also be mentioned.

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81) L. Pauling, Nature 161, 1019 (1948); Proc. Roy. Soc. A196, 343 (1949); Physica 15, 23 (1949).

82) C.A. Coulson, Proc. Int. Conf. Theor. Phys. Japan 629, (Tokyo 1953).

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It has been pointed out above that valence-bond method including polar states and molecular-orbital method including configurational interaction lead to identical results [61)], that the methods in their simple original form are rather different, and that the naive VB-method seems superior to the naive MO-method in treating correlation effects. In order to explain the peculiar behaviour of crystals like NiO, which are insulators but still have

incompletely filled bands, Mott [83] raised the question whether the simple valence bond method is particularly well suited for certain classes of crystals (insulators) and the band theory for other classes (conductors). One could think that correlation effects would be more important in insulators than in conductors, but these effects are probably just as essential in all types of crystals. This problem will be further discussed in Sec. 5

83) N.F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949).

(b) Dirac-Van Vleck Vector Model

In the study of the magnetic properties of crystals, the valence-bond method has been used in a particular form known as the Dirac-Van Vleck vector model [84]. In this approach, the spin-degeneracy problem of a many-electron

84) P.A.M. Dirac, Proc. Roy. Soc. (London) A123, 714 (1929); J.H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities" (Oxford University Press, London 1932); Phys. Rev. 45, 405 (1934).

system is investigated under the assumption that the space part is characterized by a set of orbitals a, b, c, d, ... and that one has integrated over the space coordinates. The splitting of the energy levels is then given by the eigenvalues to the spin Hamiltonian:

$$\mathcal{H}_{sp} = E_0 - 2 \sum_{i<j} J_{ij}\, \mathbf{s}_i \cdot \mathbf{s}_j , \qquad (53)$$

which works in the spin-space only; here $E_0$ is an average energy, and the coefficients $J_{ij}$ are the exchange integrals. This formalism has been successfully utilized in the spin-wave model [85] and in the theory of superexchange [86].

The original derivation was based on the assumption that the orbitals a, b, c, d, ... were all orthogonal and the entire approach has been critized by Slater [87] on this ground. The simple example of two electrons shows that, if the orbitals a and b are assumed to be orthogonal, one could neither discuss

85) H.A. Bethe, Z. Physik 71, 205 (1931); L. Hulthén, Arkiv f. mat., astr., fysik 26A, 11 (1938); P.W. Anderson, Phys. Rev. 86, 694 (1952); R. Kubo, Phys. Rev. 87, 568 (1952); F. Dyson, Phys. Rev. 102, 1217 (1956); J. van Kranendonk and J.H. Van Vleck, Revs. Modern Phys. 30, 1 (1958); F. Bopp and E. Werner, Z. Physik 151, 10 (1958); and others.

86) H.A. Kramers, Physica 1, 182 (1934); P.W. Anderson, Phys. Rev. 79, 350 (1950); for further references, see e.g. P.W. Anderson, Phys. Rev. 115, 2 (1959).

87) J.C. Slater, Revs. Modern Phys. 25, 199 (1953).

magnetic alinement nor bonding. The remedy is to use overlapping orbitals or to include polar states [88]. The "non-orthogonality catastrophe" in connection with the overlap integrals in crystal theory has previously been mentioned [61,78], and a long series of papers has now been written on this subject [89].

88) R. Serber, J. Chem. Phys. 2, 697 (1934); Phys. Rev. 45, 461 (1934).

89) J.H. Van Vleck, Phys. Rev. 49, 232 (1936); P.O. Löwdin, J. Chem. Phys. 18, 365 (1950); W.J. Carr Jr., Phys. Rev. 92, 28 (1953); Y. Mizuno and T. Izuyama, Progr. Theoret. Phys. Japan 22, 344 (1959); F. Takano, J. Phys. Soc. Japan 14, 348 (1959); T. Arai (unpublished).

It should be observed that it may be quite possible to incorporate non-orthogonality, polar states, correlation effects, etc. in the vector model in a simple way [90]. For a two-particle system, one has a singlet and a triplet state

90) P.O. Löwdin, Technical Note 46, Uppsala Quantum Chemistry Group; Revs. Modern Phys. 34, 1 (1962).

and the identity

$$\left.\begin{aligned} E &= \frac{1}{2}({}^1E + {}^3E) \pm \frac{1}{2}({}^1E - {}^3E) = \\ &= \frac{1}{2}({}^1E + {}^3E) - K \end{aligned}\right\} , \tag{54}$$

where $^1E$ and $^3E$ could be the true energies, $J$ is the exchange integral defined by (50) and (51), and $\kappa = -1$ for the singlet state $(S = 0)$ and $\kappa = +1$ for the triplet state $(S = 1)$. The quantity $\kappa$ may be considered as a spin operator which has the same eigenvalues and eigenfunctions as the operator $(\frac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2)$ and, according to (54), one obtains

$$\mathcal{H}_{op} = E_0 - 2\mathbf{s}_1 \cdot \mathbf{s}_2 \, J, \tag{55}$$

which is the spin Hamiltonian desired. The question whether this approach could be generalized to more electrons is now being investigated. If this is the case, the vector model would certainly form a good basis for a semi-empirical theory fully in line with the applications carried out so far [85, 86].

## (c) Extension of Valence-Bond Method

In chemistry, the concept of the covalent bond is of such a fundamental importance that it seems highly desirable to try to obtain a simple and useful formulation of the VB-method free of the previously mentioned mathematical difficulties connected with the overlap. As indicated in the discussion in connection with equations (48)-(51), the basic space function $\Phi = \Phi(r_1, r_2)$ in the VB-method is essentially a two-electron function, and there is no necessity of using the orbital approximation. The corresponding valence bond singlet would then have the form $\mathcal{A}\,\Phi(r_1, r_2)(\alpha_1\beta_2 - \beta_1\alpha_2)$. For a many-electron system having the bonds (ab), (cd), (ef), ... with the space functions $\Phi_{ab}$, $\Phi_{cd}$, $\Phi_{ef}$, ..., one would instead of (52) get the more general valence bond singlet

$$^1\Psi = \mathcal{A}\, \Phi_{ab}(r_1, r_2)\, \Phi_{cd}(r_3, r_4)\, \Phi_{ef}(r_5, r_6) \ldots (\alpha_1\beta_2 - \beta_1\alpha_2)(\alpha_3\beta_4 - \beta_3\alpha_4)(\alpha_5\beta_6 - \beta_5\alpha_6) \ldots, \tag{56}$$

where, in each bond function, one could include the overlap, the polar states, and the full correlation effects in each bond.

Such a two-electron extension of the valence-bond method has been worked out by Hurley, Lennard-Jones, and Pople [91]. The overlap associated

91) A. C. Hurley, J. Lennard-Jones, and J. Pople, Proc. Roy. Soc. London A220, 446 (1953).

with a specific bond does not cause any difficulties, but there is an overlap between the functions associated with different bonds which leads again to considerable mathematical complications. In order to simplify the theory, one has sometimes introduced the assumption of strong orthogonality between the bonds:

$$\int \Phi_{ab}(r_1, r_2)\ \Phi_{cd}(r_1, r_4)\ dv_1 = 0\ , \tag{57}$$

which means that the bonds to a certain extent are independent of each other. The implications of this condition have recently been studied in detail [92].

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92) T. Arai, J. Chem. Phys. 33, 95 (1960); P.O. Löwdin, J. Chem. Phys. 35, 78 (1961).

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The extended VB-method has been successfully applied to crystals: to a study of diamond by Schmid [93] and to an investigation of ZnS by Asano and Tomishina [94]. In molecular theory, this approach has become known under the name of "perfect-pairing approximation" [95].

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93) L.A. Schmid, Phys. Rev. 92, 1373 (1953); Am. J. Phys. 22, 255 (1954).

94) S. Asano and Y. Tomishina, J. Phys. Soc. Japan 11, 644 (1956).

95) See e.g. R.G. Parr, F.O. Ellison, and P.G. Lykos, J. Chem. Phys. 24, 1106 (1956); J.M. Parks and R.G. Parr, J. Chem. Phys. 28, 335 (1958); R. McWeeny and K.A. Ohno, Proc. Roy. Soc. (London) A225, 367 (1960); R. McWeeny, Revs. Modern Phys. 32, 335 (1960).

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## 4. TIGHT-BINDING APPROXIMATION

### (a) Basic Problems

The tight-binding approximation introduced in crystal theory by Bloch [12] is a band theory using the atomic orbitals of the constituents as a basis, and it corresponds in its most refined form to the ASP-MO-LCAO-SCF method in molecular theory [11,13]. The nature of the tight-binding scheme in general has been briefly discussed previously in this review and, in this section, we will concentrate our interest on some basic problems of particular importance connected with this approach. Since the valence-bond method is often based on atomic orbitals, some of the problems are common to both approaches.

<u>Approximate linear dependencies</u>. - The fundament of Ritz's method [9] for solving eigenvalue problems was discussed in Sec. 2c. If $\{f_\ell\}$ is a set of functions forming a complete basis, the Schrödinger equation is equivalent to a system of linear equations (36) with the secular determinant

$$\det\left(\mathcal{H}_{mn} - \epsilon\, \delta_{mn}\right) = 0 . \tag{58}$$

We note that, if some of the functions in the set $\{f_\ell\}$ would be linearly dependent so that $\sum_\ell f_\ell a_\ell = 0$ for some non-vanishing coefficients $a_\ell$, the rows and columns in this determinant would also be linearly dependent, which implies that the secular determinant would be <u>identically vanishing</u> for all values of the parameter $\epsilon$. In order to be able to use the secular equation for determining the eigenvalues $\epsilon$, one has thus to be sure that the functions in the basis $\{f_\ell\}$ are linearly independent.

In this connection, it is convenient to introduce a certain measure $\mu$ for the degree of linear independence defined by the minimum of the quantity

$$d = \int \Big| \sum_\ell f_\ell a_\ell \Big|^2 (dx) , \tag{59}$$

where the coefficients $a_\ell$ are subject to the auxiliary condition $\sum_\ell |a_\ell|^2 = 1$ which means that they cannot all simultaneously be vanishing. For $d$ one has the alternative form

$$d = \frac{a^\dagger \Delta\, a}{a^\dagger a} , \tag{60}$$

with the auxiliary condition removed, and we can hence draw the conclusion that $\mu$ is the smallest eigenvalue of the metric matrix $\Delta$ which is positive definite. If $\mu = 0$, the set $\{f_\ell\}$ is linearly dependent, whereas, if $\mu \neq 0$, the set is linearly independent and everything is in order, at least in the sense of ordinary mathematics.

However, in any numerical application of Ritz's method, one can use only a finite number of figures. This means that, if $\mu$ is smaller than the rounding-off error, the basic set is approximately linearly dependent, and the corresponding secular equation (58) will be identically vanishing within the accuracy used. If the quantity $\mu$ is small but not necessarily vanishing, one has often a corresponding loss of significant figures in the calculation of $\epsilon$. The occurrence of approximate linear dependencies is hence a very serious problem from practical points of view.

This problem is not limited to the tight-binding approximation but is of a very general nature [96]. An investigation of some of the standard radial

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96) P.O. Löwdin, Ann. Rev. Phys. Chem. 11, 107 (1960).

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sets $\{r^{n-1}\}$, $\{r^{n-1}e^{-r}\}$, $\{e^{-nr}\}$, $\{e^{-nr^2}\}$, etc. for $n = 1, 2, 3, \ldots$, shows that the corresponding measures $\mu$ quickly become exceedingly small, and that the sets are actually to a high extent approximately linearly dependent.

As another typical example, we will consider the set of powers $1, x, x^2, x^3, \ldots$ for $-1 \leq x \leq +1$, which is often used in studying e.g. angular behaviour with $x = \cos\theta$. From mathematics, we know that this set is complete and linearly independet, but an investigation of $\mu$ reveals that the set quickly becomes approximately linearly dependent. Since the even powers $1, x^2, x^4 \ldots$ are orthogonal to the odd powers $x, x^3, x^5, \ldots$, there are actually two orthogonal subsets which can be treated independently. The smallest eigenvalue $\mu$ of the metric matrix $\Delta$ is given in Table I as a function of the number of functions in the subset, and the result is perhaps somewhat surprising. It tells us that one has to be extremely careful in using a non-orthogonal basis $\{f_\ell\}$ in applying Ritz's method in molecular and crystal theory. Since it seems as if the remedy would be a transformation of the basis to an orthonormal set, we will continue with a brief study of such procedures.

The phenomenon of the almost identically vanishing secular equation was first observed in crystal theory by Parmenter [97] in a tight-binding study

TABLE I. Lowest eigenvalue $\mu$ of matrix $\Delta_{pq} = \langle x^p | x^q \rangle$ for the interval $-1 \leq x \leq +1$ ; n = number of members in each set. Unit= $10^{-9}$.

| Even set | | Odd set | |
|---|---|---|---|
| n | $\mu$ | n | $\mu$ |
| 2 | 79 316 688 | 2 | 33 154 158 |
| 3 | 3 275 556 | 3 | 1 254 936 |
| 4 | 117 839 | 4 | 43 655 |
| 5 | 4 002 | 5 | 1 451 |
| 6 | 131 | 6 | 45 |
| 7 | 5 | 7 | 1 |
| 8 | 1 | 8 | 1 |

**The author is indebted to F.K. Klaus Appel and F.K. Einar Lundqvist for carrying out the numerical calculations involved.**

97) R.H. Parmenter, Phys. Rev. 86, 552 (1952).

of the lithium metal using Gaussian functions as atomic orbitals.

Orthonormalization procedures. - Starting from the basis $\{f_\ell\}$ having a metric matrix $\Delta$ with the elements $\Delta_{mn} = \langle f_m | f_n \rangle$, we will now study the general linear transformation $A$ which transforms this basis to another $\{\varphi_m\}$ which is orthonormal, so that $\langle \varphi_m | \varphi_n \rangle = \delta_{mn}$. Using matrix notations, we will write the transformation in the form $\varphi = f A$, or $\varphi_m = \sum_a f_a A_{am}$. Since $\varphi^\dagger \varphi = 1$ and $f^\dagger f = \Delta$, one obtains directly the condition $A^\dagger \Delta A = 1$. Substituting $A = \Delta^{-1/2} B$, one is lead to the equation $B^\dagger B = 1$ and, since the transformation should be non-singular, $B$ is a unitary matrix. The general orthonormalization procedure has hence the form[36)]

$$\varphi = f \Delta^{-1/2} B \quad , \tag{61}$$

where $B$ is an arbitrary unitary matrix. If $A$ is chosen triangular, one obtains Schmidt's classical procedure of successive orthogonalization which is more simply derived directly. If $B$ is chosen equal to $1$, one obtains, the symmetric orthonormalization[35, 36)], in which all functions in the basis $\{f_\ell\}$ are treated in an equivalent way. In this case, it is essential to evaluate the matrix $\Delta^{-1/2}$. Putting $\Delta = 1 + S$, where $S$ is the overlap matrix of the basis, one has the formal expansion

$$\Delta^{-1/2} = (1 + S)^{-1/2} = 1 - \tfrac{1}{2} S + \tfrac{3}{8} S - \tfrac{5}{16} S^3 + - \cdots \quad , \tag{62}$$

which is convergent, if the overlap is sufficiently small, for instance $\sum_a |S_{\mu a}| < 1$. For many crystals, the series (62) is divergent, and one has then to use more forceful methods to evaluate $\Delta^{-1/2}$.

The metric matrix $\Delta$ is hermitean and positive definite, and we will let $U$ be the unitary matrix which brings it to diagonal form $d$, so that

$$U^\dagger \Delta U = d \quad , \tag{63}$$

where all the eigenvalues $d_k$ are positive and the smallest one gives the measure $\mu$ of linear independence. The matrix $\Delta^{-1/2}$ may now be defined by the relation $\Delta^{-1/2} = \mathbf{U} d^{-1/2} \mathbf{U}^\dagger$, where one can choose e.g. the positive square roots in $d^{-1/2}$. With this definition of $\Delta^{-1/2}$ one can prove some interesting theorems [98] about the set $\varphi = f\,\Delta^{-1/2}$. It has further been shown [99] that, if the basis $\{f_\ell\}$ undergoes a unitary transformation $\mathbf{R}$ then the set $\{\varphi_\ell\}$ undergoes the same transformation.

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98) G.W. Pratt Jr., and S.F. Neustadter, Phys. Rev. 101, 1248 (1956); B.C. Carlson and J.M. Keller, Phys. Rev. 105, 102 (1957); P.G. Lykos and H.N. Schmeising, J. Chem. Phys. 35, 288 (1961).

99) J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954).

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It is clear that, unless the series (62) is rapidly convergent, the calculation of the matrix $\Delta^{-1/2}$ is a cumbersome procedure, particularly for a crystal. Using the Chebyshev polynomials, one has recently obtained a considerable simplification of this problem by deriving a closed expression [100] for the elements of $\Delta^{-1/2}$ for an infinite (periodic) chain and, by using perturbation technique, the same method can be extended to three dimensions.

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100) P.O. Löwdin, R. Pauncz, and J. de Heer, J. Math. Phys. 1, 461 (1960).

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In discussing the symmetric orthonormalization, we have assumed that the basis $\{f_\ell\}$ is linearly independent, so that $\mu \neq 0$ and $\Delta^{-1/2}$ exists. In order to treat also the case of exact and approximate linear dependencies, it is convenient to choose $\mathbf{B} = \mathbf{U}$ in (61), which leads to the <u>canonical orthogonalization</u> [101] $\varphi = f\,\mathbf{U}\, d^{-1/2}$ or

$$\varphi_k = d_k^{-1/2} \sum_\alpha f_\alpha U_{\alpha k} , \tag{64}$$

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101) P.O. Löwdin, Advances in Physics 5, 1 (1956), p. 49-56.

which formula is valid for all $d_k \neq 0$. It may be convenient to arrange this set according to decreasing values of $d_k$; the sum of the absolute squares of the coefficients in (64) equals $d_k^{-1}$, and the set (64) has an optimum property in this connection.

This means that, even if one goes over to an orthonormal set, the approximate linear dependencies will still show up in the calculations: the sum of the absolute squares of the coefficients in the last function will be $\mu^{-1}$, i.e. the coefficients will usually be very large at the same time as they have a small number of significant figures. However, formula (64) gives us at least a possibility of refining the calculations within a certain accuracy by striking away those functions $\varphi_k$ as correspond to too small eigenvalues $d_k$, but the completeness of the basis is then gone. The finite number of bits of our electronic computers (or desk machines, etc.) puts us hence in a dilemma, which has not yet been solved.

In conclusion, it should be added that, in crystal theory, it is often highly convenient to use one more method, namely the <u>successive orthonormalization of groups</u> of functions. Let $\xi$ and $\eta$ represent two groups of functions having the metric matrix

$$\begin{pmatrix} 1 & S \\ S^\dagger & 1 \end{pmatrix}, \tag{65}$$

where $S = \xi^\dagger \eta$ is a quadratic or rectangular matrix. We will leave the first group $\xi$ unchanged and replace the second group by a linear combination $\zeta = \xi A + \eta B$. The orthogonality condition $\xi^\dagger \zeta = 0$ gives $A = -SB$, whereas the orthonormality condition $\zeta^\dagger \zeta = 1$ leads to $B^\dagger (1 - S^\dagger S) B = 1$ with the solution $B = (1 - S^\dagger S)^{-1/2}$. The result is hence

$$\xi = \xi, \qquad \zeta = (\eta - \xi S)(1 - S^\dagger S)^{-1/2}, \tag{66}$$

which is a generalization of the standard Schmidt procedure to groups of functions. Formula (66) is useful, for instance, in deriving the orthogonalized plane waves or in handling groups of orthogonalized atomic orbitals.

Orthonormalization problem in crystal theory. - The orthonormalization problem takes a very interesting form in crystal theory depending on the translational symmetry of the lattice. Let $\Phi(\mathbf{r})$ be an arbitrary atomic orbital, i.e. a localized function centered around a certain lattice point which we may have chosen as the origin, and let $\boldsymbol{\Phi}$ denote the set of all such orbitals $\Phi(\mathbf{r}-\mathbf{m})$ centered around the equivalent points $\mathbf{m}$ in the lattice. This set has a metric matrix $\boldsymbol{\Delta} = \boldsymbol{\Phi}^{\dagger}\boldsymbol{\Phi}$ with the elements:

$$\Delta(\mathbf{m},\mathbf{n}) = \int \Phi^{*}(\mathbf{r}-\mathbf{m})\,\Phi(\mathbf{r}-\mathbf{n})\,(dv), \tag{67}$$

which is cyclic and which is hence brought to diagonal form by the unitary transformation

$$U(\mathbf{m},\mathbf{k}) = G^{-3/2}\, e^{2\pi i\,\mathbf{k}\cdot\mathbf{m}} \tag{68}$$

The eigenvalues of $\boldsymbol{\Delta}$ are then given by the formula

$$d(\mathbf{k}) = \sum_{\mathbf{m}}^{(G)} e^{2\pi i\,\mathbf{k}\cdot\mathbf{m}}\,\Delta(0,\mathbf{m}) \; . \tag{69}$$

Instead of the original set $\boldsymbol{\Phi}$, we can now introduce a set $\boldsymbol{\varphi}$ of orthonormalized AO's by the symmetric procedure $\boldsymbol{\varphi} = \boldsymbol{\Phi}\boldsymbol{\Delta}^{-1/2}$. Here the matrix $\boldsymbol{\Delta}^{-1/2}$ may be evaluated by various methods, of which at the present stage the Chebyshev expansion method [100] is probably the most forceful.

It is also of interest to consider the canonical orthonormalization procedure defined by (64). Using (68) and (17), we find that this approach leads directly to the standard Bloch-functions associated with the set $\boldsymbol{\Phi}$ in a properly normalized form.

The Bloch functions can actually be derived from the given atomic orbital $\Phi(\mathbf{r})$ in several ways. According to (20), one can start from a single orbital $\Phi(\mathbf{r})$ and resolve this function into its Bloch components

$$\Phi(\mathbf{r}) = \sum_{\mathbf{k}}^{(G)} \Phi(\mathbf{k},\mathbf{r}) , \tag{70}$$

$$\Phi(\mathbf{k},\mathbf{r}) = O_{\mathbf{k}}\,\Phi(\mathbf{r}) = G^{-3}\sum_{\mathbf{m}}^{(G)} e^{2\pi i\,\mathbf{k}\cdot\mathbf{m}}\,\Phi(\mathbf{r}-\mathbf{m}) , \tag{71}$$

where $\Phi(\mathbf{k}, \mathbf{r})$ is an unnormalized Bloch function of the standard type [12]. Of course, one could also think of this Bloch function as being formed by linear combinations of the atomic orbitals in the various lattice points (LCAO). The different aspects may be valuable in different connections.

Bloch functions associated with different $\mathbf{k}$ -values are orthogonal, whereas they are usually not normalized. The normalization integral for the function (71) takes the form

$$\langle \Phi | O_{\mathbf{k}} | \Phi \rangle = G^{-3} d(\mathbf{k}) , \tag{72}$$

but the best way of normalizing the Bloch functions is probably to take the Bloch projections (multiplied by $G^{+3/2}$) of the orthonormalized AO's, $\varphi = \Phi \Delta^{-1/2}$, where the matrix $\Delta^{-1/2}$ is evaluated e.g. by Chebyshev technique. All the $G^3$ Bloch functions will then be normalized at once, whereas one otherwise has to carry out one normalization for each one of the $G^3$ $\mathbf{k}$ - values. Valuable information may also be obtained by combining the two approaches.

It is remarkable that the LCAO Bloch-functions formed from the orthogonalized AO's $\varphi$ except for the normalization are completely identical [102] with those formed from the original AO's $\Phi$. This is a special case of a general <u>invariance theorem</u>, saying that the Bloch projection of any linear combination

$$\Phi'(\mathbf{r}) = \sum_{\mathbf{m}}^{(G)} A(\mathbf{m}) \, \Phi(\mathbf{r}-\mathbf{m}) , \tag{73}$$

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102) P.O. Löwdin, J. Chem. Phys. 18, 365 (1950); Advances in Physics 5, 1 (1956), p. 53; R.G. Parr, J. Chem. Phys. 33, 1184 (1960).

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with arbitrary coefficients $A(\mathbf{m})$ will, except for a normalization factor, be identical with the corresponding Bloch projection of the function $\Phi(\mathbf{r})$. According to (19), one has

$$T(\mathbf{m}) \, O_{\mathbf{k}} = O_{\mathbf{k}} \, T(\mathbf{m}) = e^{2\pi i \, \mathbf{k} \cdot \mathbf{m}} \, O_{\mathbf{k}} , \tag{74}$$

and applying $O_{\mathbf{k}}$ to $\Phi'$, we obtain

$$\mathcal{O}_{k}\, \Phi'(r) = \mathcal{O}_{k} \left[ \sum_{m}^{(G)} A(m) T(-m) \right] \Phi(r) = \\ = \left[ \sum_{m}^{(G)} A(m)\, e^{-2\pi i k \cdot m} \right] \mathcal{O}_{k}\, \Phi(r) , \tag{75}$$

which proves the theorem. In this connection, the projection technique is hence very convenient.

Completeness problem in tight-binding scheme. - It has been discussed in various connections, whether the atomic orbitals would form a sufficient basis for band theory or whether something essential is missing in the tight-binding method. It is evident that, if one introduces a complete set of AO's in every lattice point $m$, the basis will be highly overcomplete, and the key problem will be to eliminate the redundancies connected with the linear dependencies. If, on the other hand, one introduces a truncated set of AO's in each lattice point, the treatment may be disturbed by approximate linear dependencies at the same time as some essential element may be missing.

From theoretical point of view, it is sufficient to introduce a complete set of AO's $\{f_\ell\}$ in a single lattice point, since we may then use expansion (34), i.e. $\Psi_k = \Sigma f_\ell c_\ell$. In studying the Bloch functions, we can apply the projection operator $O_k$ and go over from (34) to (37), i.e.

$$\psi_k = \sum_\ell (O_k f_\ell)\, c_\ell , \tag{76}$$

which relation says that it is possible to express every Bloch function associated with the wave vector $k$ in terms of the subset $(O_k f_\ell)$. From the completeness of $\{f_\ell\}$ follows hence the completeness of $\{O_k f_\ell\}$ with respect to the subspace characterized by $k$. Consequently, nothing can be missing.

However, if one uses a set of hydrogen-like orbitals 1s, 2s, 2p, 3s, 3p, 3d, .... and constructs the corresponding Bloch functions, one will find a peculiarity in analyzing these functions in terms of plane waves [101]: once the orbitals for neighbouring atoms start having large overlap, the main contribution to the Bloch function will come from the first Brillouin zone. Except for the region around the nucleus, the Bloch functions will then become more and more similar to a free wave associated with the first zone, and little new

will be obtained by adding more $(n\ell)$-functions. One should remember, however, that the higher functions contribute to the description of the inner parts of the atoms, and that a particularly important part comes from the continuum, which is necessary to make the basis $\{f_\ell\}$ complete.

If one neglects the continuum in the tight-binding approximation, one is certainly leaving out a very important part of the basis. It is true that the handling of the continuum functions may cause some mathematical difficulties, but these are easily circumvented if one follows Schrödinger's suggestion [103]

[103] E. Schrödinger, Ann. Physik 79, 361 (1926).

and uses a set which is both entirely discrete and complete; such a set is easily derived from the hydrogen-like orbitals by omitting the principal quantum number n in the radial variable $\rho = 2Zr/n$. These new functions $\overline{1s}$, $\overline{2s}$, $\overline{2p}$, $\overline{3s}$, $\overline{3p}$, ... will be more localized within the atomic cell of interest, they will give more details concerning the ion core and the nuclear region, at the same time as the higher orbitals will give Bloch functions which are close to free waves. The set of modified atomic orbitals has proven to be extremely useful in atomic and molecular theory [104], and it will probably be just as valuable in crystal theory.

[104] H. Shull and P.O. Löwdin, J. Chem. Phys. 23, 1362 (1955); 25, 1035 (1956); 30, 617 (1959); E. Holøien, Phys. Rev. 104, 1301 (1956); Proc. Phys. Soc. A71, 357 (1958); J.O. Hirschfelder and P.O. Löwdin, Molecular Physics 2, 229 (1959).

One could ask how an orthonormal set of Block functions should best be constructed in the tight-binding scheme to give a basis which is in principle complete and which does not contain any linear dependencies. If $\{f_\ell\}$ denotes the set of modified atomic orbitals in a single lattice point, the projected subsets $\{O_k f_\ell\}$ associated with different reduced wave vectors $k$ are certainly mutually orthogonal and non-interacting with respect to $H_{eff}$, but the individual functions within each subset $\{O_k f_\ell\}$ are neither normalized nor orthogonal. Since the functions $\overline{1s}$, $\overline{2s}$, $\overline{2p}$, $\overline{3s}$, $\overline{3p}$, $\overline{3d}$, ... form a natural sequence, the functions within each subset $\{O_k f_\ell\}$ are conveniently transformed by means of successive orthonormalization. If only a limited number of points in $k$-space will be studied, this is a procedure which is easily carried out by considering one $k$-value at a time.

However, if it is desirable to derive a complete set of Bloch functions which are orthonormal within all the $G^3$ subsets associated with the reduced wave vector $\mathbf{k}$, it is simpler to start by deriving a complete set of atomic orbitals orthonormalized over all the lattice points. In such a case, one starts by considering the functions in all the lattice points and carries out a symmetric orthogonalization according to (61) with $\mathbf{B} = \mathbf{1}$, proceeds in the same way with all the functions $\overline{2s}$, with all the functions $\overline{2p}$, .... etc. one type at a time. This procedure seems physically feasible, since all the lattice points are treated in an equivalent way. It leads to a sequence of groups of orthonormalized atomic orbitals, which are then made mutually orthogonal by means of the successive orthogonalization obtained by repeated use of formula (66). In each lattice point, one gets in this way, a set of orthonormal atomic orbitals $\overline{1s}'$, $\overline{2s}'$, $\overline{2p}'$, $\overline{3s}'$, $\overline{3p}'$, ... which are translationally connected and altogether complete. Finally, one forms the Bloch projections

$$G^{+3/2}\, O_{\mathbf{k}}\, (\overline{n\ell m})', \tag{77}$$

which constitute the orthonormal, complete set desired. Each Bloch function is here characterized by the reduced wave vector $\mathbf{k}$ and an index corresponding to the atomic quantum numbers $(n\, \ell\, m)$.

By using the invariance theorem (71), it may be shown that the two ways of proceeding here described actually lead to identical result. For the moment, it seems simpler to construct the complete set of translationally connected atomic orbitals $\overline{1s}'$, $\overline{2s}'$, $\overline{2p}'$, $\overline{3s}'$, ... since one can use the Chebyshev technique [100] for evaluating the $(-\frac{1}{2})$ power of a cyclic matrix in both steps of the procedure, but, of course, it should be possible to find the corresponding short-cut also in the other approach.

By constructing a complete orthonormal set of Bloch functions of the type (77), one can hence remove two weak points in the tight-binding approximation, namely the occurrence of approximate linear dependencies and the incompleteness particularly with respect to the inner region around each lattice point otherwise arising from the neglect of the continuum.

## (b) Recent Applications

For applications of the tight-binding approximation to crystal theory, we will again refer to the previously mentioned reviews by Löwdin [23], Herman [24], and Pincherle [25] and comment only on some recently published papers.

The relation between the MO-LCAO method in molecular theory and the tight-binding scheme in crystal theory can be particularly well studied in connection with the graphite problem, where one can start out from a single six-membered ring as in the benzene molecule, add more and more rings until one obtains a graphite layer, and finally add the layers to a three-dimensional crystal. The electronic structure of graphite, its diamagnetism and other properties have successfully been studied in this way [105].

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105) See e.g. C.A. Coulson and R. Taylor, Proc. Phys. Soc. (London) A65, 815 (1952); D.F. Johnston, Proc. Roy. Soc. (London) A237, 48 (1956); M. Yamasaki, J. Chem. Phys. 26, 930 (1957); J.W. McClure, Phys. Rev. 108, 612 (1957); R.R. Haering, Can. J. Phys. 36, 352 (1958); S. Mase, J. Phys. Soc. Japan 13, 563 (1958); J.C. Slonczewsky and P.R. Weiss, Phys. Rev. 109, 272 (1958); T.E. Peacock and R. McWeeny, Proc. Phys. Soc. (London) 74, 385 (1959); H. Sato, J. Phys. Soc. Japan 14, 609 (1959); J. Kontechý and M. Tomášek, Phys. Rev. 120, 1212 (1960).

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In connection with diamond-type crystals, the work by Schmid [93] using VB-method has previously been mentioned, and here we will only add a study by Morita [106], where he uses a semi-localized crystal orbital method.

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106) A. Morita, Progr. Theoret. Phys. 19, 534 (1958).

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Among the papers on boron crystals, we would like to mention an extensive investigation of the electronic structure and band properties of the metal borides of type $MB_6$ carried out by Flodmark [107], and a study of boron

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107) S. Flodmark, Arkiv f. Fysik 9, 1357 (1955); 11, 417 (1957); 14, 513 (1959); Svensk Kemisk Tidsk. 70, 12 (1958).

carbide by Yamasaki [108].

108) M. Yamasaki, J. Chem. Phys. 27, 746 (1957).

The oxide ionic crystals offer an interesting problem [109], and Yamashita [110] has now extended his previous work to a study of the oxygen band in magnesium oxide, whereas O'Sullivan [111] has treated beryllium oxide.

109) J. Yamashita and M. Kojima, J. Phys. Soc. Japan 7, 261 (1952).

110) J. Yamashita, Phys. Rev. 111, 733 (1958).

111) W. O'Sullivan, J. Chem. Phys. 30, 379 (1959).

The tight-binding studies of the alkali hydrides and alkali halides are being continued. The covalent character of lithium hydride has been investigated by Morita and Takahashi [112] using semi-localized crystal orbitals, whereas the

112) A. Morita and K. Takahashi, Progr. Theoret. Phys. 19, 257 (1958).

behaviour of this crystal under very high pressure has been treated by Behringer [113]. The electronic structure of the alkali halides has been studied by Grimley [114] with particular attention to lithium fluoride. Howland [115] has finally carried through a careful study of the band structure and cohesive properties of potassium chloride.

113) R.E. Behringer, Phys. Rev. 113, 787 (1959).

114) T.B. Grimley, Proc. Phys. Soc. (London) 70, 123 (1957); 71, 749 (1958).

115) L.P. Howland, Phys. Rev. 109, 1927 (1958).

The ionic crystals with constituents having completely filled shells are remarkable from the point of view that the naive MO-method and the naive VB-method lead to identical results with respect to all properties which may be

derived from the total wave function. These crystals are also particularly convenient for a study by means of the tight-binding approximation, and a rather fixed approach seems finally to have been established. In this connection, we would like to make some critical comments on the conventional interpretation of the data obtained in calculating e.g. the cohesive energy.

### (c) Virial Theorem in Theory of Ionic Crystals

The classical theory of ionic crystals developed by Madelung and Born was based on the fundamental assumption that the essential constituents of such a crystal are the positively and negatively charged ions. The system of ions was assumed to be in equilibrium under the influence of two types of potentials: an attractive potential, corresponding to the electrostatic interaction between the ions as point charges and represented by a Madelung energy, and a repulsive potential, for which Born and Landé suggested the inverse power $C r^{-n}$ and later Born and Mayer the exponential $C \exp(-r/\rho)$.

A characteristic feature of this model is that the Madelung energy forms the dominating part of the cohesive energy of the crystal. In a recent investigation [116], it has been pointed out, however, that the cohesive energy actually consists of several large terms of the same order of magnitude as the Madelung contribution, and that the kinetic energy plays a very important role in this connection.

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116) A. Fröman and P.O. Löwdin, Technical Note 51, Uppsala Quantum Chemistry Group (1960); J. Phys. Chem. Solids 20, ... (1961).

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The ratio between the kinetic energy $\langle T \rangle$ and the potential energy $\langle V \rangle$ is determined by the virial theorem [117] which, for a system with only coulombic interactions, takes the special form $\langle T \rangle = -\frac{1}{2} \langle V \rangle$, or $\langle T \rangle = -E$, $\langle V \rangle = +2E$, where $E$ is the total energy, $E = \langle T + V \rangle$. For an ionic crystal, the virial theorem is satisfied in this simple form both for the equilibrium state $(R = R_0)$ and for the free ions $(R \approx \infty)$, here indicated by an index f (= free).

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117) E.A. Hylleraas, Z. Physik 54, 347 (1929); V. Fock, Z. Physik 63, 855 (1930). For more complete references, see P.O. Löwdin, J. Mol. Spectroscopy 3, 46 (1959).

The cohesive energy $E_{coh}$ is defined as the difference between the total energy $E_o$ of the crystal in its ground state and the energy $E_f$ of the free constituents, so that $E_{coh} = E_o - E_f$. The change in kinetic energy $\Delta T$ and the change in potential energy $\Delta V$ are further defined by the relations:

$$\Delta T = T_o - T_f \quad , \qquad \Delta V = V_o - V_f \tag{78}$$

and, using the virial theorem for both states, we hence obtain

$$\Delta T = -E_{coh} \quad , \qquad \Delta V = +2E_{coh} \tag{79}$$

These relations show that the kinetic energy increases under the formation of a solid, whereas the potential energy decreases twice as much leaving a balance equal to the cohesive energy: $\Delta T + \Delta V = E_{coh}$. The kinetic energy of a bound state is hence considerably larger than the kinetic energy of the free constituents, which to a certain extent are excited or "promoted" [118] in a compound.

118) K. Rüdenberg, Revs. Modern Phys. 34, .... (1962); in press.

In Table II, we have gathered the values of the cohesive energy for some of the alkali halides obtained empirically by means of the Born-Haber cycle. We have further listed $\Delta T$ according to (79) whereas $\Delta V$ has been divided into two terms: the Madelung energy $V_{Mad}$, and the remaining potential energy $V_{ext}$ which must necessarily depend on the extension of the ions. The last term is negative and of the same order as the Madelung energy.

Because of the kinetic energy term, which here contains also a small contribution from the nuclear motion, the interpretation is certainly strikingly different from the conventional one. It may be shown [116] that the quantum-mechanical calculations of the cohesive energy of the alkali halides carried out so far on the basis of the tight-binding approximation, by means of an adjustable scale factor [117], may be brought in complete agreement with this picture. However, the simple Born-Mayer model has certainly also to be modified to fulfil the requirement of the virial theorem.

TABLE II. Interpretation of the cohesive energy of some alkali halides according to Fröman and Löwdin, /J. Phys. Chem. Solids 20, .... (1961)/.

$\Delta T$ = Increase in kinetic energy in formation of solid

$\Delta V$ = Decrease in potential energy in formation of solid

Units: kcal/mole

| Crystal | $E_{coh}$ | $\Delta T$ | $\Delta V = V_{Mad} + V_{ext}$ | |
|---|---|---|---|---|
| | | | $V_{Mad}$ | $V_{ext}$ |
| LiF | -244.4 | 244.4 | -291.0 | -197.8 |
| NaF | -216.3 | 216.3 | -240.6 | -192.0 |
| KF | -192.1 | 192.1 | -219.5 | -164.7 |
| RbF | -184.4 | 184.4 | -208.0 | -160.8 |
| LiCl | -201.7 | 201.7 | -228.1 | -175.3 |
| NaCl | -184.4 | 184.4 | -208.0 | -160.8 |
| KCl | -167.9 | 167.9 | -186.3 | -149.5 |
| RbCl | -162.1 | 162.1 | -179.4 | -144.8 |
| LiBr | -191.3 | 191.3 | -213.0 | -169.6 |
| NaBr | -175.9 | 175.9 | -196.8 | -155.0 |
| KBr | -161.0 | 161.0 | -178.6 | -143.4 |
| RbBr | -155.8 | 155.8 | -171.5 | -140.1 |
| LiI | -179.3 | 179.3 | -195.1 | -163.5 |
| NaI | -165.5 | 165.5 | -181.4 | -149.6 |
| KI | -152.3 | 152.3 | -166.3 | -138.3 |

## 5. EXTENSION OF BAND THEORY; DIFFERENT ORBITALS FOR DIFFERENT SPINS

As mentioned earlier in this review, it has been pointed out by Slater, Pauling, Mott, and others that the naive valence bond method is superior to the ordinary band theory in treating correlation effects and particularly that the former leads to a correct asymptotic behaviour of the energy curve for separated atoms; compare Fig. 1. On the other hand, band theory has many advantages in describing conductivity and similar properties, and the question is whether it is possible to combine the advantages of the two approaches by a synthesis of the two ideas. This can be done by a generalization of band theory which removes part of the correlation error discussed in Sec. 2d.

Extended Hartree-Fock scheme. - The large correlation errors in the conventional Hartree-Fock scheme depend undoubtedly on the fact that pairs of electrons of opposite spins are forced together in doubly filled orbitals. This electron pairing goes back partly to the classical formulation of Pauli's exclusion principle, partly to the fact that this procedure permits a simple construction of Slater determinants as pure eigenfunctions to the total spin, $S^2$ and $S_z$. One can apparently remove a large part of the correlation error by letting electrons with different spins occupy different orbitals in space, so that they get a possibility to avoid each other; compare the discussion of the "Coulomb hole" in Sec. 2d.

The idea of this orbital splitting comes originally from Hylleraas [119] who used it in treating the helium atom, and it was intensely discussed for two--electron systems at the Shelter Island Conference [120] in 1951. There is an

119) E.A. Hylleraas, Z. Physik 54, 347 (1929); C. Eckart, Phys. Rev. 36, 878 (1930).

120) M. Kotani, Proc. Shelter Island Conf., 139 (1951); G.R. Taylor and R.G. Parr, Proc. Nat. Acad. Sci. U.S. 38, 154 (1952); J.E. Lennard--Jones, Phil. Mag. 43, 581 (1952); R.S. Mulliken, Proc. Nat. Acad. Sci. U.S. 38, 160 (1952).

obvious difficulty in generalizing the idea to a many-electron system depending on the fact that, if one permits different orbitals for different spins, the corresponding Slater determinant will no longer be a pure spin state.

By means of a simple projection operator technique, the Slater determinant $D = (N!)^{-\frac{1}{2}} \det\{\psi_1, \psi_2, \psi_3, \ldots \psi_N\}$ may uniquely be resolved into pure spin components ${}^{(2S+1)}D$, which are orthogonal and non-interacting with respect to the total Hamiltonian (7), so that

$$D = \sum_S {}^{(2S+1)}D , \tag{80}$$

where one should sum over all values of S involved. The component of the specific multiplicity (2S+1) is selected by means of a projection operator of the form

$${}^{(2S+1)}O = \prod_{k}^{k \neq S} \frac{S^2 - k(k+1)}{S(S+1) - k(k+1)} , \tag{81}$$

which annihilates all components except the one desired, which survives the operation in an unchanged form. The operator O fulfills the relations $O^2 = O$, $O^\dagger = O$, $S^2 O = S(S+1)\,O$ and its properties have been studied in detail [121].

[121] P.O. Löwdin, Phys. Rev. 97, 1509 (1955); Coll. Int. Centre Nat. Rech. Sci. 82, 23 (Paris, 1958); Technical Note 12, Uppsala Quantum Chemistry Group (1958).

It is now possible to introduce an extension of the Hartree-Fock scheme by considering a total wave function which is approximated by the component of the Slater determinant D which has the pure spin desired, so that

$${}^{(2S+1)}\underline{\Psi} = {}^{(2S+1)}O\,D . \tag{82}$$

If the basic spin-orbitals $\psi_1, \psi_2, \psi_3, \ldots \psi_N$ in D are subject to a linear transformation, this wave function is changed only by a constant. This implies that the Fock-Dirac density matrix $\rho$ defined by (4) will be the fundamental invariant of the theory, which determines all physical properties. Since the

projection (81) will affect only the spin functions, it is clear that the total wave function $\Psi$ will depend only on the two space density matrices $\rho_+(r_1, r_2)$ and $\rho_-(r_1, r_2)$ which are contained in $\rho$ :

$$\rho(x_1, x_2) = \rho_+(r_1, r_2)\,\alpha_1\alpha_2 + \rho_-(r_1, r_2)\,\beta_1\beta_2 \,. \tag{83}$$

For the expectation value of the Hamiltonian one obtains

$$\langle \mathcal{H}_{op} \rangle_{Av} = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle D | \mathcal{H} O | D \rangle}{\langle D | O | D \rangle} \,, \tag{84}$$

where one has used the turn-over-rule and the relation $O^2 = O$. The variation principle $\delta < H > = 0$ leads to the best possible density matrices $\rho_+$ and $\rho_-$, or to the corresponding best spin-orbitals. The approach may be characterized as an <u>extended Hartree-Fock scheme</u> [122], which preserves the simple physical visuality of the one-electron-model but still removes a very large fraction of the total correlation error.

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122) P.O. Löwdin, Nikko Symp. Mol. Phys., 13 (Maruzen, Tokyo 1954); Phys. Rev. <u>97</u>, 1509 (1955); Proc. 10th Solvay Conference, 71 (1955); Revs. Modern Phys. <u>32</u>, 328 (1960).

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The general treatment of the extended Hartree-Fock theorem is greatly simplified by the existence of a <u>pairing theorem</u> with respect to the orbitals in $\rho_+$ and $\rho_-$. Let $u_1, u_2, \dots u_m$ and $v_1, v_2, \dots v_n$ be the orbitals contained in $\rho_+$ and $\rho_-$, respectively. Each set may be chosen orthonormal and, in addition, there exists two unitary transformations $\mathbf{U}$ and $\mathbf{V}$, so that the two transformed sets $\mathbf{u}' = \mathbf{u}\mathbf{U}$, $\mathbf{v}' = \mathbf{v}\mathbf{V}$ fulfil the relation

$$\langle u_k' | v_l' \rangle = \lambda_k \delta_{kl} \,. \tag{85}$$

This implies that, without loss of generality, the orbitals may be chosen so that each orbital in $\rho_+$ is orthogonal to all orbitals in $\rho_-$, except possibly one to which it is <u>paired</u> with an overlap integral $\lambda_k$ fulfilling the inequality

$0 < \lambda_k < 1$ . If $m > n$, the extra orbitals in $\varrho_+$ may always be chosen orthogonal to all orbitals in $\varrho_-$ . The proof follows simply by considering the quadratic or rectangular overlap matrix $\mathbf{S} = \mathbf{u}^\dagger \mathbf{v}$ of order $m \times n$ and the unitary transformations $\mathbf{U}$ and $\mathbf{V}$ bringing the hermitean matrices $\mathbf{S}\mathbf{S}^\dagger$ and $\mathbf{S}^\dagger\mathbf{S}$ respectively, to diagonal form. The pairing theorem introduces far-reaching orthogonality simplifications in the calculations and makes it possible to evaluate the energy in (84) in a straight-forward way.

The solution of the ordinary Hartree-Fock equations for a molecular or crystal system is a very complicated matter, and one can expect that the treatment of the extended equations will be still more difficult. An ab initio calculation of $\varrho_+$ and $\varrho_-$ would certainly give valuable information about the mutual behaviour of electrons having antiparallel spins, but, for the moment one has to be satisfied with highly approximate solutions based on suitable trial functions and a few adjustable parameters. In choosing the trial functions, one is to a certain extent guided by the idea that "electrons with different spins do try to avoid each other", but the justification of the entire approach is the energy lowering finally obtained. In connection with the orbital splitting, one speaks of "in-out effect", "right- and left-effect", "up-and down-effect", "alternant effect", etc., but only the last idea will be briefly discussed here.

Alternant Crystal Orbital Method. - In this section, we will consider an extension of the ordinary band theory which is inspired by certain aspects of the valence bond method. Again it is convenient to explain the idea by starting from the hydrogen molecule. If a and b are the atomic orbitals involved, the molecular orbital wave function and the valence bond wave function are actually represented by the anti-symmetric singlet components of the Hartree-products $(a_1 + b_1)(a_2 + b_2)\alpha_1\beta_2$ and $a_1 b_2 \alpha_1 \beta_2$, respectively; see Fig. 2. In addition, we may now consider the antisymmetric singlet component of the Hartree--product $u_1 v_2 \alpha_1 \beta_2$, where u and v are semi-localized molecular orbitals [123] given by the expression

$$u = a\cos\vartheta + b\sin\vartheta\ , \qquad v = a\sin\vartheta + b\cos\vartheta\ . \tag{86}$$

123) C.A. Coulson, and I. Fischer, Phil. Mag. 40, 386 (1949).

When $\vartheta = 0$, one obtains the naive VB-method, whereas for $\vartheta = 45^\circ$ one gets

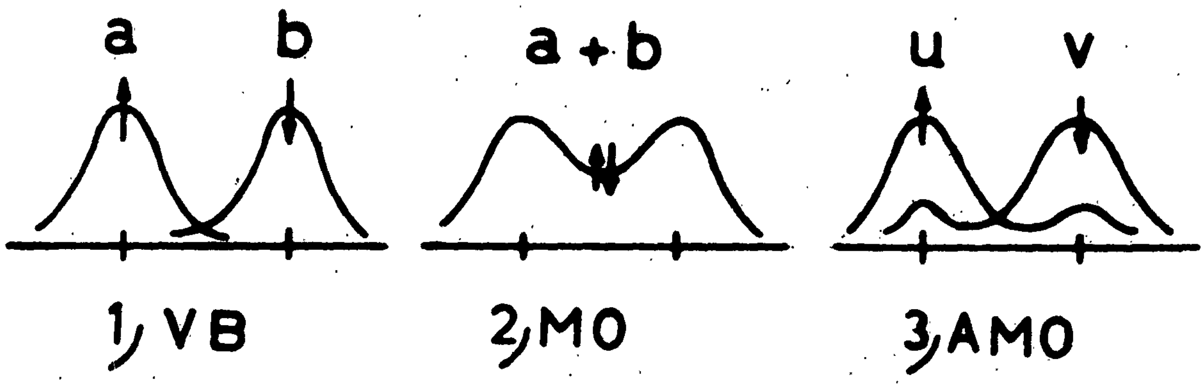


Fig. 2. Comparison between the arrangements of orbitals and spins in the valence bond method 1), the molecular--orbital method 2), and the alternant molecular-orbital method 3); $H_2$-molecule.

the naive MO-method. The parameter $\vartheta$ gives us hence a possibility of a continuous transition from one type of theory to the other; it measures the degree to which the two electrons would like to avoid each other, and $\vartheta$ may hence be denoted as the "correlation angle". A value of $\vartheta$ intermediate between 0 and $45^{\circ}$ corresponds to a valence-bond method including polar states, to a molecular-orbital method including configuration interaction, or to an extended MO-approach along the lines sketched above.

For a valence crystal, one could now think of an extended Hartree-Fock scheme in terms of localized orbitals [124], where $\rho_+$ and $\rho_-$ are

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124) Compare references 41 and 42, with respect to the ordinary Hartree-Fock method.

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such that each pair $(u_k, v_k)$ would be associated with a specific valence bond. Because of the relation (85), there may then be a close connection between the general pairing theorem in the extended Hartree-Fock scheme and the orthogonality assumption (57) in the extended valence bond method or "perfect-pairing" approximation discussed in Sec. 3c.

Let us now consider a simple crystal with a half-filled conduction band, like the alkali metals. The ordinary band theory is here affected by a considerable correlation error which is particularly accentuated in the wrong behaviour of the singlet energy curve for separated atoms; see Fig. 1 (page 29) and the discussion in Sec. 2d. In his classical 1930 paper, Slater [61] has studied this problem in connection with the body-centered cubic sodium metal, and he pointed out that it seemed desirable to find a modification of the ordinary MO-theory which, for separated atoms, would go over into some form of VB-treatment based on the idea that the electrons with antiparallel spins would separate, so that the electrons with plus spin would occur in the "corners" and the electrons with minus spin in the "centers" of the lattice; see Fig. 3. The advantage of such a spin arrangement would be that it would prevent the formation of negative ions, which is the cause of the wrong asymptotic behaviour of the energy curve. We will now try to realize and generalize this idea.

The body-centered cubic lattice is a special type of an important class of crystals which is called alternant systems, and which is characterized by the fact that all lattice points may be divided into two equivalent, interpenetrating

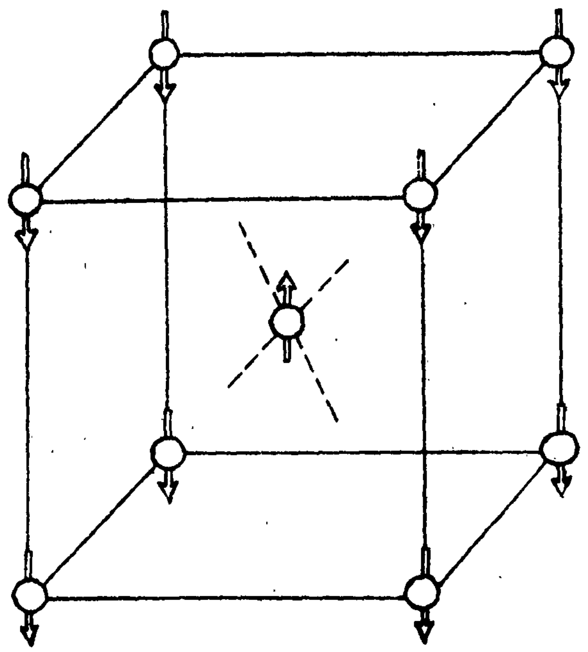

**Fig. 3. Spin arrangement for separated atoms in body-centered cubic lattice of sodium metal.**

sublattices (I) and (II). The sublattice (II) is supposed to contain the origin and will be called the even sublattice, whereas (I) will be called the odd sublattice. In order to obtain an extension of the ordinary band theory, we will now try to introduce alternant crystal orbitals which are semi-localized on the two sublattices, and let electrons with plus spin tend to be associated with sublattice (I) and those with minus spin associated with sublattice (II).

For this purpose, we will consider the space of the reduced wave vector $\mathbf{k}$ and all points which are situated within the Fermi-surface of ordinary band theory. Instead of the single Bloch projection operator $O_{\mathbf{k}}$ defined by (17):

$$O_{\mathbf{k}} = G^{-3} \sum_{\mathbf{m}}^{(G)} e^{2\pi i \mathbf{k}\cdot\mathbf{m}} \, T(-\mathbf{m}) \quad . \tag{87}$$

It is now convenient to introduce the two partial sums over the two sublattices:

$$\begin{aligned} O_{\mathbf{k}I} &= G^{-3} \sum_{\mathbf{m}}^{(I)} e^{2\pi i \mathbf{k}\cdot\mathbf{m}} \, T(-\mathbf{m}) \\ O_{\mathbf{k}II} &= G^{-3} \sum_{\mathbf{m}}^{(II)} e^{2\pi i \mathbf{k}\cdot\mathbf{m}} \, T(-\mathbf{m}) \; , \end{aligned} \tag{88}$$

each one containing $G^3/2$ terms, and the splitting operators:

$$\begin{aligned} Q_{\mathbf{k}I} &= \sqrt{2}\, ( \cos\vartheta \, O_{\mathbf{k}I} + \sin\vartheta \, O_{\mathbf{k}II} ) \; , \\ Q_{\mathbf{k}II} &= \sqrt{2}\, ( \sin\vartheta \, O_{\mathbf{k}I} + \cos\vartheta \, O_{\mathbf{k}II} ) \; . \end{aligned} \tag{89}$$

These operators will work, for instance, on an atomic orbital $\varphi(\mathbf{r})$ situated around the origin and will give rise to a set of alternant crystal orbitals with one pair for each $\mathbf{k}$ -value. For $\vartheta = 45^\circ$, there will be no splitting and the functions within each pair will be identical and equal to ordinary Bloch functions. For $\vartheta = 0$, there will be a complete splitting and delocalization of each pair on the two sublattices involved, in accordance with Slater's idea [61].

The operators (88) and (89) are all hermitean and satisfy some simple algebraic relations which are useful in the applications. One has $O_I^2 = \frac{1}{2}O_{II}$, $O_{II}^2 = \frac{1}{2}O_{II}$, $O_I O_{II} = O_{II} O_I = \frac{1}{2}O_I$, where for simplicity we have omitted the index $\mathbf{k}$ . This gives further

$$\begin{aligned} Q_I^2 = Q_{II}^2 &= O_{II} + \sin 2\vartheta \cdot O_I \; , \\ Q_I Q_{II} = Q_{II} Q_I &= O_I + \sin 2\vartheta \cdot O_{II} \; , \end{aligned} \tag{90}$$

which relations are used in calculating the normalization integrals and the overlap within the pair.

We note that the splitting operators $Q$ are not eigenfunctions to all three primitive translations but that they always fulfil the relation:

$$T(\mathbf{m})\, Q_{I,II} = e^{2\pi i\, \mathbf{k}\cdot\mathbf{m}}\, Q_{I,II} \,, \tag{91}$$

where $\mathbf{m}$ is a general translation from one point in a sublattice to an equivalent point within the same sublattice. From this property follows also the general orthogonality relation:

$$Q_{I,II}(\mathbf{k}) \cdot Q_{I,II}(\boldsymbol{\ell}) = 0 \,, \qquad \mathbf{k} \neq \boldsymbol{\ell} \,, \tag{92}$$

which says that the splitting operators applied to a function $\varphi(\mathbf{r})$ will render us a set of alternant crystal orbitals satisfying the pairing theorem (85). For each point $\mathbf{k}$, there is hence an overlapping pair which is orthogonal towards all other pairs. This property greatly simplifies the applications of the theory.

The basic Slater determinant D is now constructed by assigning $\alpha$-spin to orbitals of type I and $\beta$-spin to orbitals of type II for all points $\mathbf{k}$ within the Fermi surface, so that the electrons are permitted to avoid each other. One takes the projection (82) and evaluates the energy expectation value according to (84), and the best value of the "correlation angle" $\vartheta$ and the best form of $\varphi(\mathbf{r})$ are then determined by means of the variation principle $\delta < H > = 0$.

It is evident that an important generalization of this approach is possible by letting the correlation angle $\vartheta$ be a function of the reduced wave vector $\mathbf{k}$ :

$$\vartheta = \vartheta(\mathbf{k}) \,, \tag{93}$$

where the form of the function could again be determined by the variation principle [125].

125) In comparison to some earlier work, references 121 and 122, a change of notation $\vartheta = 45^{\circ} - \theta$ should be observed. Even $\theta$ was previously characterized as "correlation angle".

It is remarkable, however, that a large improvement can be obtained by using a single parameter $\vartheta$ and particularly that a correct asymptotic behaviour of the singlet energy curve for separated atoms can be achieved by observing that $\vartheta$ approaches $0^\circ$. For $\vartheta = 0^\circ$, one gets purely alternant orbitals which are completely delocalized on the two sublattices and, by a proper choice of $\varphi(r)$ they can be made strictly orthogonal. In this case [121], the energy (84) takes the simple form:

$$\langle \mathcal{H}_{op} \rangle_{Av} = \int D^* \mathcal{H} D \,(dx) - \frac{2S(S+1) - N}{N^2} \sum_{j,k} \langle j\mathrm{I}, k\mathrm{II} \,|\, \frac{e^2}{r_{12}} \,|\, k\mathrm{II}, j\mathrm{I} \rangle , \qquad (94)$$

where the latter term goes to zero for separated atoms and, since there is no accumulation of negative ions, the energy curve gets the correct asymptotic behaviour. Of still larger importance are probably the improvements which can be obtained for the equilibrium state $(R = R_0)$.

This approach has so far been essentially tested only for molecules, where actually the difficulties connected with forming the projection (80) are particularly accentuated. In an investigation of the benzene molecule, Itoh and Yoshizumi [126] obtained $\vartheta \approx 22^\circ$ and could show that about 85 o/o of the previously known correlation energy could be removed, and this result has recently been improved by de Heer [127] using two parameters $\vartheta$. The approach has further proven to be valuable in a study of the alternating spin densities in odd alternant hydrocarbon radicals [128]. It has been used successfully for investigating the correlation properties in the finite and infinite linear chain [129] with the idea of making applications to conjugated systems; studies of three--dimensional crystals are now in progress.

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126) T. Itoh and H. Yoshizumi, J. Phys. Soc. Jap 10, 201 (1955); J. Chem. Phys. 23, 412 (1955); Busseiron Kenkyu 83, 13 (1955).

127) J. de Heer (private communication).

128) R. Lefebvre, H.H. Dearman, and H.M. McConnell, J. Chem. Phys. 32, 176 (1960).

129) R. Pauncz, J. de Heer, and P.O. Löwdin, Technical Notes 55 and 56, Uppsala Quantum Chemistry Group (1960); J. Chem. Phys. ...

Actually, it seems easier to use the alternant orbital method for treating crystals and very large molecules rather than small molecules. The reason is that the effect of the projection (2) becomes simpler for large N. By using some of the previous results [130], one can easily show that, for a

130) See particularly equations (15)-(24) in P.O. Löwdin, Phys. Rev. 97, 1509 (1955).

finite value of S and $\Psi = {}^{(2S+1)}D$ one obtains

$$\lim_{N\to\infty} \langle \mathcal{H}_{op} \rangle_{Av} = \lim_{N\to\infty} \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle D | \mathcal{H} | D \rangle}{\langle D | D \rangle}, \tag{95}$$

i.e. the energy of the spin component ${}^{(2S+1)}D$ is the same as the energy of the determinant D itself. It is clear that, for a very large N, a single spin flip or a finite number of flips cannot influence the total energy, so that the singlet, triplet, quintet,... etc. all have the same energy in this case. The determinant D contains also higher spin states with S/N finite, but it follows from (94) that they occur in such a small portion that they do not contribute to the average energy of the mixture for $N = \infty$. A detailed study of the spin components in D is now being carried out in Uppsala.

Formula (95) indicates that, for large N, the variation with respect to the starting function $\varphi(\mathbf{r})$ and the correlation parameter (93) may be carried out as if the total wave function would simply be the Slater determinant D. However, the singlet wave function is, of course, still represented by the singlet projection of D, which ensures that the wave function is invariant under the transformation $\alpha \leftrightarrow \beta$ and that the spin density is identically zero everywhere in space.

It should be mentioned that there are some similarities between this approach and the unrestricted Hartree-Fock scheme developed by Slater and his collaborators [131]. It was pointed out by Slater that, in a system with un-

131) J.C. Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951); Revs. Modern Phys. 25, 199 (1953); R.K. Nesbet, Proc. Roy. Soc. A230, 312 (1955); G.W. Pratt Jr., Phys. Rev. 102, 1303 (1956); J.H. Wood and G.W. Pratt Jr., Phys. Rev. 107, 995 (1957); R.K. Nesbet and R.E. Watson, Ann. Phys. 9, 260 (1960); L.M. Sachs, Phys. Rev. 117, 1504 (1960); R.E. Watson and A.J. Freeman, Phys. Rev. 120, 1125 (1960); Phys. Rev. 120, 1134 (1960).

balanced spins having $S_z \neq 0$, the electrons with plus spin and those with negative spin would be influenced by different exchange potentials. One could hence expect that electrons with different spins would have different orbitals, and this effect was called exchange polarization. In order to study this effect, Slater approximated the total wave function by a single determinant with different orbitals for different spins. Many important results have been obtained so far by this approach, particularly with respect to magnetic behaviour [131]. For a detailed comparison between the unrestricted and the extended Hartree--Fock schemes, we will refer to a recent paper [132].

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132) P.O. Löwdin, Ann. Acad. Reg. Sci. Upsaliensis 2, 127 (1958).

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The main result of this section is that one can obtain an essential lowering of the total energy of a Slater determinant D by permitting "different orbitals for different spins". For $S_z = 0$, there will be a considerable orbital splitting due to correlation and, for $S_z \neq 0$ there may be an additional exchange polarization. The basic equations are the same as in the original Hartree-Fock scheme characterized by (1)-(5), but no symmetry restrictions are imposed on the spin-orbitals involved. Instead the symmetry properties are handled by a component analysis of the determinant [133].

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133) If this component analysis is omitted, one may obtain results which look paradoxical. Compare the giant spin waves in A.W. Overhauser, Phys. Rev. Letters 4, 415, 462 (1960), and the criticism by W. Kohn and S.J. Nettel, Phys. Rev. Letters 5, 8 (1960); K. Sawada and N. Fukuda, Progr. Theoret. Phys. 25, 653 (1961); T. Arai, Argonne Report 1961 (unpublished).

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In this way, it seems possible to obtain an extension of band theory which preserves the physical simplicity of the conventional method but has an essential part of the correlation error removed. For a schematic survey of the advantages and disadvantages of the ordinary band theory, the valence bond method, and the combined approach outlined here in the form of a table, we will refer to another paper [90].

## 6. GENERAL SELF-CONSISTENT-FIELD THEORY AND EXACT SOLUTION TO MANY-ELECTRON PROBLEM

For a long time, the Hartree-Fock scheme was considered as the essential and ultimate theoretical tool for understanding the independent-particle-model from the point of view of many-particle theory. The scheme was successfully applied to the electronic clouds of the atoms and their shell structure, to the mobile $\pi$-electrons of the conjugated compounds in organic chemistry, and to the band structure of crystals. One believed that the qualitative and to a certain extent also quantitative success of the scheme depended on the fact that the interactions between the electrons were comparatively weak, and that the correlation effects could be considered as a small perturbation.

The picture was completely changed with the discovery that the independent-particle-model seemed to work extremely well also for the atomic nuclei in the so-called nuclear shell-model. Here the explanation could hardly be that the forces were weak, and it seemed necessary to find an extension of the independent-particle-model which would work also for strong interactions between the particle. Such an extension has been developed by Brueckner [134)]

134) K.A. Brueckner, C.A. Levinson, and H.M. Mahmoud, Phys. Rev. 95, 217 (1954); K.A. Brueckner, Phys. Rev. 96, 508 (1954); 97, 1353 (1955); 100, 36 (1955); K.A. Brueckner and C.A. Levinson, Phys. Rev. 97, 1344 (1955); H.A. Bethe, Phys. Rev. 103, 1353 (1956); J. Goldstone, Proc. Roy. Soc. (London) A239, 267 (1957); H.A. Bethe and J. Goldstone, Proc. Roy. Soc. (London) A238, 551 (1957); L.S. Rodberg, Ann. Phys. 2, 199 (1957); to mention only a selection of the rich literature on this subject.

and his collaborators. The new scheme is based on the use of a scattering or reaction operator, where the correlation between any two particles is exactly included, whereas the correlation between three and more particles is neglected. This so-called Brueckner approximation works very well for nuclear matter, since the forces are of such a short-range nature.

For an electronic system, the situation is a little bit different, since the Coulomb forces are of such a long-range nature that it may be necessary to include also the correlation between three and more electrons. This is ultimately a question of order of magnitude and depends also on the accuracy

desired. Here we will briefly show that it is possible to extend the line of development which goes from Hartree-Fock to Brueckner still further and relate the exact formal solution of the many-electron Schrödinger equation to the independent-particle-model through a self-consistent-field scheme containing "average" potentials [135].

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135) P.O. Löwdin, Technical Notes 47 and 48, Uppsala Quantum Chemistry Group (1960).

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Partitioning Technique for Solving Schrödinger Equation. - One of the strongest tools for solving the Schrödinger equation $H\Psi = E\Psi$ in one-electron or many-electron theory is rendered by the partitioning technique, since it contains many of the conventional methods as special cases [136]. The technique is also convenient to explain the projection operator formalism that we are actually going to use to solve the many-electron problem.

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136) For references, see P.O. Löwdin, Technical Note 11, Uppsala Quantum Chemistry Group (1958) /unpublished/.

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In applying Ritz's expansion method discussed in Sec. 2c, we will introduce a complete orthonormal basis $\{f_\ell\}$ and write the eigenfunction in the form $\Psi = \sum_\ell f_\ell c_\ell$, where the coefficients $\{c_\ell\}$ form a column vector $\mathbf{c}$. The system (36) may then be written in the condensed matrix form

$$\mathbf{H}\mathbf{c} = E\mathbf{c}, \tag{96}$$

which is simply the transform of the original Schrödinger equation in the discrete representation introduced. Let us now divide or "partition" the complete basis $\{f_\ell\}$ into two subsets (a) and (b), so that the set (a) contains a finite number of functions. The matrix $\mathbf{H}$ and the vector $\mathbf{c}$ may then be written in the form

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{aa} & \mathbf{H}_{ab} \\ \mathbf{H}_{ba} & \mathbf{H}_{bb} \end{pmatrix}, \quad \mathbf{c} = \begin{pmatrix} \mathbf{c}_a \\ \mathbf{c}_b \end{pmatrix}, \tag{97}$$

and equation (96) may be written as two equations:

$$\begin{aligned} \mathbf{H}_{aa}\mathbf{c}_a + \mathbf{H}_{ab}\mathbf{c}_b &= E\,\mathbf{c}_a , \\ \mathbf{H}_{ba}\mathbf{c}_a + \mathbf{H}_{bb}\mathbf{c}_b &= E\,\mathbf{c}_b , \end{aligned} \tag{98}$$

Solving $\mathbf{c}_b$ from the last equation, one obtains

$$\mathbf{c}_b = (E\cdot\mathbf{1}_{bb} - \mathbf{H}_{bb})^{-1}\,\mathbf{H}_{ba}\mathbf{c}_a , \tag{99}$$

and substitution of this expression into the first equation gives

$$\overline{\mathbf{H}}_{aa}\mathbf{c}_a = E\,\mathbf{c}_a \tag{100}$$

$$\overline{\mathbf{H}}_{aa} \equiv \mathbf{H}_{aa} + \mathbf{H}_{ab}(E\cdot\mathbf{1}_{bb} - \mathbf{H}_{bb})^{-1}\,\mathbf{H}_{ba} \tag{101}$$

Equation (100) has exactly the same form as the original equation (96), but the total matrix $\mathbf{H}$ is now condensed into a finite matrix $\overline{\mathbf{H}}_{aa}$ defined by (101). This technique enables us to concentrate our interest on a certain subset (a), whereas the influence of the other subset (b) may be considered as a "perturbation" represented by the second term in (101). The partitioning technique may be used in many different theoretical connections, and it is also an excellent tool for the numerical solution of secular equations of very high orders[137]. It is then often convenient to choose the subset (a) as consisting of a single element, and the method will still render both discrete and degenerate eigenvalues without any difficulty.

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137) P.O. Löwdin, Adv. Chem. Phys. 2, 207 (Interscience, New York 1959), p. 270 f.

<u>Projection Operator Formalism.</u> - In this section, we will rewrite the partitioning technique in a slightly more abstract form. Let $\mathcal{O}$ be the projection operator which selects the subspace (a) of order $g$ so that

$$\mathcal{O}^2 = \mathcal{O} , \quad \mathcal{O}^\dagger = \mathcal{O} , \quad \mathrm{Tr}(\mathcal{O}) = g . \tag{102}$$

The operator $P = 1 - \mathcal{O}$ satisfies the relations $P^2 = P$, $P^+ = P$ and $\mathcal{O}P = P\mathcal{O} = 0$, and it is apparently the projection operator for the subspace (b), which we will characterize as the "orthogonal complement" to the subspace (a).

Let us start by considering a non-degenerate level $E$ and choose $g = 1$. Let further $\Phi$ be an arbitrary trial function with a non-vanishing projection $\mathcal{O}\Phi = \varphi$, which we will normalize so that $\langle \varphi | \varphi \rangle = 1$, i.e. $\langle \Phi | \mathcal{O} | \Phi \rangle = 1$. For the eigenfunction $\Psi$, satisfying $(H - E)\Psi$, one has the identity

$$\begin{aligned} \Psi &= (\mathcal{O}+P)\Psi = \varphi + PK^{-1}K\Psi = \\ &= \varphi + PK^{-1}[K + P(\mathcal{H}-E)(\mathcal{O}+P)]\Psi = \\ &= \varphi + PK^{-1}P\mathcal{H}\varphi + PK^{-1}[K - P(E-\mathcal{H})P]\Psi . \end{aligned} \tag{103}$$

Here $K$ is an arbitrary non-singular operator which will now be chosen so that we get rid of the last term in (103). We will introduce the definitions

$$K = P(E-\mathcal{H})P ; \qquad T = PK^{-1}P . \tag{104}$$

In matrix notation, we would say that $K$ represents the (bb)-"corner" of the matrix $(E\,\mathbf{1} - \mathbf{H})$, and that $T$ is the "inverse of the corner"; see <u>Fig. 4.</u> In the following, we will often, instead of the full definition $T = P[P(E - H)P]^{-1}P$ use the symbolic notation

$$T = \frac{P}{E-\mathcal{H}} , \tag{105}$$

but we have to remember its full meaning. It is clear that $T$ satisfies the relations

$$\mathcal{O}T = T\mathcal{O} = 0 , \qquad P(E-\mathcal{H})T = P , \tag{106}$$

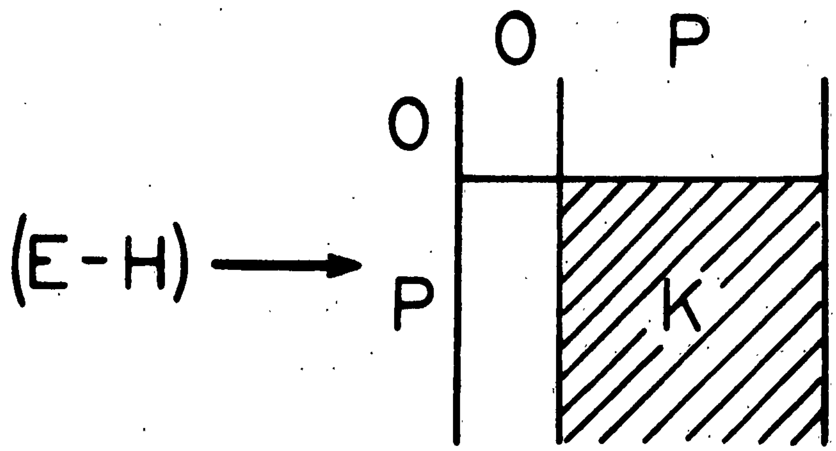


Fig. 4. Partitioning of energy matrix.

which we will often use in the following. From (103), we obtain

$$\underline{\Psi} = \varphi + T\mathcal{H}\varphi = (\mathcal{O} + T\mathcal{H}\mathcal{O})\,\Phi \,, \tag{107}$$

which relation is analogous to (99). Of special interest is now the operator

$$\Omega = \mathcal{O} + T\mathcal{H}\mathcal{O} \,, \tag{108}$$

since this operator applied to any trial function $\Phi$ will give an exact solution $\Psi = \Omega\,\Phi$ , provided that $\mathcal{O}\Phi \neq 0$. This result indicates that $\Omega$ is an eigen-operator to $H$ , i.e. that

$$\mathcal{H}\Omega = E\,\Omega \,, \tag{109}$$

and it is further easily seen that $\Omega^2 = \Omega$ . It should be observed that $\Omega$ , which consists of an idempotent term $\mathcal{O}$ and a nil-potent term $TH\mathcal{O}$ does not commute with its adjoint operator $\Omega^+$ and it is hence not a normal operator. It may be characterized as a non-normal projection operator, and its importance comes from its connection with $\infty$-order perturbation theory.

From (109) follows further $\mathcal{O}(H - E)\Omega = \mathcal{O}H\mathcal{O} + \mathcal{O}HTH\mathcal{O} - \mathcal{O}E\mathcal{O} = 0$ , and the energy relation:

$$\mathcal{O}E\mathcal{O} = \mathcal{O}(\mathcal{H} + \mathcal{H}T\mathcal{H})\,\mathcal{O} \,. \tag{110}$$

Multiplying to the left and right by $\Phi$ and integrating, we obtain

$$E = \langle \varphi \,|\, \mathcal{H} + \mathcal{H}\frac{P}{E - \mathcal{H}}\mathcal{H} \,|\, \varphi \rangle \,, \tag{111}$$

which relation corresponds to the well-known Schrödinger-Brillouin formula [138]

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138) L. Brillouin, J. Phys. radium (7) <u>33</u>, 373 (1932); E. Wigner, Math. naturw. Anz. ungar. Akad. Wiss. <u>53</u>, 477 (1935).

in perturbation theory; the latter may be derived from (111) by expanding the inverse $T$ by means of a power-series expansion. The corresponding wave function is given by (107) and fulfills the normalization $\langle \varphi \mid \Psi \rangle = 1$. Because of this connection, the projection operator formalism based on $\Omega$ is equivalent to $\infty$-order perturbation theory.

In (111) the eigenvalue problem is given in an implicit form $E = f(E)$, where

$$f(E) \equiv \langle \varphi \mid \mathcal{H} + \mathcal{H} \frac{P}{E-\mathcal{H}} \mathcal{H} \mid \varphi \rangle, \tag{112}$$

$$f'(E) = -\langle \varphi \mid \mathcal{H} \frac{P}{(E-\mathcal{H})^2} \mathcal{H} \mid \varphi \rangle = -\langle T\mathcal{H}\varphi \mid T\mathcal{H}\varphi \rangle \tag{113}$$

It is natural to try to solve this problem by a first-order iteration procedure based on the formula $E^{(k+1)} = f\{E^{(k)}\}$, and which leads to a series of values $E^{(0)}, E^{(1)}, E^{(2)}, \ldots$. Putting $E^{(k)} = E + \epsilon^{(k)}$ and using the mean-value theorem $f\{E + \epsilon^{(k)}\} = f(E) + \epsilon^{(k)} f'\{E + \theta\epsilon^{(k)}\}$ with $0 < \theta < 1$, one obtains

$$\epsilon^{(k+1)} = \epsilon^{(k)} f'\{E + \theta\epsilon^{(k)}\} \tag{114}$$

Since $f'$ is always negative, the errors $\epsilon^{(k)}$ will alternate in sign, which implies that the successive values $E^{(k)}$ will alternately be upper and lower bounds to $E$. Hence we have the <u>bracketing theorem</u> that between two consecutive values in the series $E^{(0)}, E^{(1)}, E^{(2)}, \ldots$ there will always be at least one eigenvalue. The procedure will be convergent if $|f'| < 1$ and divergent if $|f'| > 1$.

A much faster convergence can be obtained by going over to a second-order iteration procedure, e.g. by solving the equation $y \equiv E - F(E) = 0$ by the Newton-Raphson process:

$$E^{*} = E^{(0)} - \frac{y^{(0)}}{y'^{(0)}} = E^{(0)} - \frac{E^{(0)} - E^{(1)}}{1 - f'\{E^{(0)}\}} \tag{115}$$

It should be observed that the right-hand member is identical with the standard variational expression in quantum mechanics. It is easily shown that this process is always convergent.

Connection with Schrödinger Perturbation Theory. - Let us now consider the case, when $H = H_0 + V$ where $V$ is an arbitrary weak or strong perturbation. We will assume that $\Theta$ is now the eigenoperator to $H_0$ associated with the level $E_0$ under consideration, so that $H_0\Theta = \Theta H_0 = E_0\Theta$. In other words, $\Theta$ will project out the unperturbed eigenfunction $\varphi_0$. We note that we need here only one single eigenfunction to $H_0$ and not the complete spectrum, which is an essential simplification; the orthogonal complement to $\varphi_0$ characterized by $P$ may be obtained by orthogonalizing any complete set towards $\varphi_0$. From (106), (108), and (110) follows directly

$$\Omega = (1 + TV)\Theta, \qquad (116)$$
$$\Theta E \Theta = \Theta(E_0 + V + VTV)\Theta .$$

Of particular interest is here the operator

$$t = V + VTV , \qquad (117)$$

which is called the reaction operator associated with the perturbation $V$, the unperturbed Hamiltonian $H_0$, and the state under consideration. Using (116), we obtain

$$E = E_0 + \langle \varphi_0 | t | \varphi_0 \rangle , \qquad (118)$$

showing that the expectation value of the reaction operator $t$ with respect to the unperturbed state gives the true energy shift. Substitution into (117) gives finally

$$t = V + V \frac{P}{(E_0 - \mathcal{H}_0) - (V - \langle t \rangle_0)} V , \qquad (119)$$

which is the basic formula for the reaction operator in our theory. There is again an iterative element, which may be handled in the same way as before. It would be tempting to comment on the linked-cluster expansion and related problems on the basis of this formula, but it would take us too far in this connection, and instead we would like to refer to some forthcoming publications. The

essential thing for the moment is that the exact reaction operator has been defined.

Self-Consistent-Field Theories. - In order to review some of the common features of the SCF-theories, we will consider a total many-particle Hamiltonian of the form

$$\mathcal{H}_{op} = \mathcal{H}_{(0)} + \sum_i \mathcal{H}_i + \sum_{i<j} \mathcal{H}_{ij} + \sum_{i<j<k} \mathcal{H}_{ijk} + \cdots \qquad (120)$$

Here $H_{(0)}$ is a constant, which may be of importance from the point of view of convergence [15] but which plays no role in the interaction between the particles, so that it may temporarily be omitted. Let us divide this Hamiltonian into two parts $H = H_0 + V$ where

$$\mathcal{H}_0 = \sum_i (\mathcal{H}_i + u_i), \qquad (121)$$

$$V = -\sum_i u_i + \sum_{i<j} \mathcal{H}_{ij} + \sum_{i<j<k} \mathcal{H}_{ijk} + \cdots, \qquad (122)$$

and $u_i$ are one-particle potentials at our disposal. The eigenvalue problem connected with $H_0$ is separable, and we obtain

$$\varphi_0 = \psi_1(x_1)\,\psi_2(x_2) \ldots \psi_N(x_N), \qquad (123)$$

where

$$(\mathcal{H}_i + u_i)\,\psi_i = \epsilon_i\,\psi_i, \qquad (124)$$

$$E_0 = \sum_i \epsilon_i \qquad (125)$$

At first, we will leave the antisymmetry requirement aside. In the so-called Hartree scheme, the total wave function is actually approximated by the simple product (123). The best one-particle functions $\psi_i$ are determined by the variation principle $\delta \langle H \rangle = 0$, which leads to Hartree equations of type (124), with Hartree potentials given by the following expressions:

$$\mathcal{U}_i = \mathcal{U}_i^{(2)} + \mathcal{U}_i^{(3)} + \mathcal{U}_i^{(4)} + \cdots ;$$

$$\mathcal{U}_i^{(2)} = \sum_{j \neq i} (\psi_j | \mathcal{H}_{ij} | \psi_j), \tag{126}$$

$$\mathcal{U}_i^{(3)} = \frac{1}{2!} \sum_{j,k \neq i}{}' (\psi_j \psi_k | \mathcal{H}_{ijk} | \psi_j \psi_k),$$

where the upper index $k$ indicates the order of the interaction term in the Hamiltonian, from which the effective potential has been derived. For the total energy, one obtains

$$\langle \mathcal{H}_{op} \rangle_{Av} = \sum_i \langle \psi_i | \mathcal{H}_i + \tfrac{1}{2} \mathcal{U}_i^{(2)} + \tfrac{1}{3} \mathcal{U}_i^{(3)} + \cdots + \tfrac{1}{N} \mathcal{U}_i^{(N)} | \psi_i \rangle =$$
$$= \langle \varphi_0 | \sum_i \left( \mathcal{H}_i + \tfrac{1}{2} \mathcal{U}_i^{(2)} + \tfrac{1}{3} \mathcal{U}_i^{(3)} + \cdots + \tfrac{1}{N} \mathcal{U}_i^{(N)} \right) | \varphi_0 \rangle, \tag{127}$$

which means that $\langle H_{op} \rangle$ is not identical with $E_o$ ; actually the factor $(1/k)$ connected with $u_i^{(k)}$ prevents the k-body interaction to be counted $k$ times as it would be in $E_o = \sum_i \epsilon_i$ .

In addition to $\varphi_o$ , we will consider the "singly excited" function $\varphi_{s.e.}$ , which is obtained from $\varphi_o$ by replacing one (and only one) of the functions $\psi_k$ by another $\bar{\psi}_k$ which is assumed to be orthogonal to the former, so that $\langle \bar{\psi}_k | \psi_k \rangle = 0$ . Using (122) and (126), one obtains directly

$$\langle \varphi_{s.e} | V | \varphi_0 \rangle = 0 , \tag{128}$$

which is a form of Brillouin's theor saying that all matrix elements of the perturbation $V$ between the basic function $\varphi_o$ and all singly excited functions will vanish identically. Since $V = H_{op} - H_o$ , one gets further

$$\langle \varphi_{s.e.} | \mathcal{H}_{op} | \varphi_0 \rangle = 0 . \tag{129}$$

We note that this relation does not prevent the singly excited functions to appear in the expansion of the exact solution, since they may come in through couplings with terms which are at least doubly excited.

After this introduction, we will discuss the <u>exact SCF-theory</u> connected with the product (123). For this purpose, we will assume that we have the potentials $u_i$ at our disposal and introduce the projection operator $\Theta$ connected

with $H_0$ and $\varphi_0$. According to (118), the exact energy is now given by the expression $E = E_0 + \langle \varphi_0 | t | \varphi_0 \rangle$, where the reaction operator $t$ is defined by (119). It must be possible to write $t$ in the form

$$\begin{aligned} t &= -\sum_i u_i + \tau = \\ &= -\sum_i u_i + \sum_{i<j} \tau_{ij} + \sum_{i<j<k} \tau_{ijk} + \cdots , \end{aligned} \tag{130}$$

where we have separated out the one-particle part $-\sum_i u_i$ and denoted the interaction part by $\tau$; the latter consists of a two-particle term, a three-particle term, etc. The total energy can now be written in the form

$$E = \langle \varphi_0 | \mathcal{H}_0 + t | \varphi_0 \rangle = \langle \varphi_0 | \sum_i \mathcal{H}_i + \tau | \varphi_0 \rangle . \tag{131}$$

This expression is, in principle, exact and cannot be improved by variation. However, in order to get a connection with the Hartree-scheme, we will now remove the coupling between $\varphi_0$ and $\tau$ and consider $\tau$ as a <u>fixed</u> given operator. The expression (131) is then no longer invariant, and the best function $\varphi_0$ is determined by equations of type (123) and (124) with potentials $u_i$ given by the conditions:

$$\begin{aligned} u_i &= u_i^{(2)} + u_i^{(3)} + u_i^{(4)} + \cdots ; \\ u_i^{(2)} &= \sum_{j \neq i} (\psi_j | \tau_{ij} | \psi_j) , \\ u_i^{(3)} &= \frac{1}{2!} \sum_{j,k \neq i}{}' (\psi_j \psi_k | \tau_{ijk} | \psi_j \psi_k) , \\ &\ldots \ldots \ldots \ldots \end{aligned} \tag{132}$$

i.e. exactly the same relations as (126) but with the interaction terms from the Hamiltonian replaced by the reaction terms from $\tau$. This gives finally

$$E = \langle \varphi_0 | \sum_i \left( \mathcal{H}_i + \tfrac{1}{2} u_i^{(2)} + \tfrac{1}{3} u_i^{(3)} + \cdots + \tfrac{1}{N} u_i^{(N)} \right) | \varphi_0 \rangle , \tag{133}$$

in complete analogy with (127).

The SCF-potentials are here considerably more complicated than in the Hartree-scheme, but the energy (133) is also the true energy containing all correlation effects. They may be calculated by a SCF-procedure based on the following "flow diagram":

$$\begin{tikzcd}
 & V \arrow[r] & t \arrow[r] & \tau \arrow[dr] & \\
\mathcal{U}_i \arrow[ur] \arrow[r] & (\mathcal{H}_i + \mathcal{U}_i) \arrow[rr] & & \psi_i \arrow[r] & \mathcal{U}_i \arrow[llll, bend left]
\end{tikzcd} \tag{134}$$

Each cycle is here more complicated than the corresponding cycle (5), since it involves the evaluation of the reaction operator $t$. This step corresponds actually to an exact solution of the Schrödinger equation, which it ought to be sufficient to carry out only once. There exists hence probably a short-cut, perhaps by means of the first-order density matrix, and research on this point is in progress.

Instead of (128) in the Hartree scheme, one obtains here directly

$$\langle \varphi_{s.e.} | t | \varphi_0 \rangle = 0 \quad , \tag{135}$$

This theorem has the important consequence that, if the exact wave function $\Psi$ is expanded in terms of Hartree products built up from the basic orbitals $\psi_1, \psi_2, \ldots \psi_N$ and their orthogonal complement, the leading term will be $\varphi_o$, and the expansion will further contain only terms which are at least doubly excited with respect to $\varphi_o$ [135]. This theorem is of importance in calculating expectation values of one-particle operators, and it gives a certain physical significance also to the "model" function $\varphi_o$.

It is now possible to follow the line from Hartree by way of Brueckner to the exact SCF-theory. Apparently, the degree of accuracy depends on how one has approximated the interaction part $\tau$ of the reaction operator $t$, and one has:

$$\text{Hartree:} \quad \mathcal{T} \approx \sum_{i<j} \mathcal{H}_{ij} + \sum_{i<j<k} \mathcal{H}_{ijk} + \cdots ;$$

$$\text{Brueckner} \quad \mathcal{T} \approx \sum_{i<j} \mathcal{T}_{ij} ; \tag{136}$$

$$\text{Exact SCF-theory} \quad \mathcal{T} = \sum_{i<j} \mathcal{T}_{ij} + \sum_{i<j<k} \mathcal{T}_{ijk} + \cdots .$$

Symmetry Requirements in SCF-Theories. - In discussing correlation effects, the symmetry requirements are certainly highly important. In the theory of fermions, the antisymmetry requirement connected with Pauli's exclusion principle diminishes the original correlation error connected with the Hartree--product with about 50 o/o, since it eliminates the main part of the correlation error connected with particles having parallel spins. In Sec. 5, we have seen that the proper use of spin projection operators for certain systems may remove another 85 o/o of the correlation error associated with electrons having antiparallel spins, so that actually only about 1/12 of the original error has to be accounted for by real many-particle theory. Hence it is highly desirable to incorporate the symmetry properties in the SCF-theories.

The antisymmetry property for fermions is easily included by means of the antisymmetry projection operator:

$$\mathcal{O}_{AS} = (N!)^{-1} \sum_{P} (-1)^{p} P , \tag{137}$$

and, instead of the total Hilbert space spanned by the complete set $\{f_\ell\}$, we will now consider only the antisymmetric subspace spanned by the subset $\{O_{AS} f_\ell\}$. Instead of starting from the Hartree product (123), we will now base our study on the corresponding Slater determinant.

The Hartree-Fock scheme is characterized by potentials of the type (126), but the interaction terms are now multiplied by reduced antisymmetrization operators, so that

$$\begin{aligned} \overline{\mathcal{H}}_{ij} &= \mathcal{H}_{ij} (1 - P_{ij}) , \\ \overline{\mathcal{H}}_{ijk} &= \mathcal{H}_{ijk} \sum_{P}^{3!} (-1)^{p} P_{ijk} , \end{aligned} \tag{138}$$

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and this introduces an essential simplification in the definitions of the Hartree--Fock potentials $u_i$, since one can now take away the restrictions $j \neq i$, $j \neq k \neq i, \ldots$ in (126) and sum over all indices. This implies that the Hartree--Fock potentials will be the same for all particles, and that these potentials are conveniently expressed in terms of the fundamental invariant $\rho$ -defined by (4).

In the <u>exact SCF-theory</u>, we can now confine our interest to the antisymmetric subspace alone, and, within this subspace, we can now repeat the partitioning procedure and evaluate the corresponding reaction operator $t$. It appears that the previous reaction terms $\tau_{ij}$, $\tau_{ijk}$, ... will be modified according to (138), so that one can remove the summation restriction in (132) and base the entire discussion on the fundamental invariant $\rho$. In this respect, the introduction of the exchange terms simplifies the structure of the SCF-theory.

In Sec. 2b, we studied the consequences of the translational symmetry of a crystal, and the same type of discussion can now be repeated here. It turns out that the basic spin-orbitals should be Bloch-functions, that the fundamental invariant $\rho$ has translational symmetry (31), and that these properties are <u>self-consistent</u> and lead to an exact wave function which is an eigenfunction to the total translations $\mathcal{T}_\nu$. This means that the important concepts connected with the space of the <u>reduced wave vector</u> $\mathbf{k}$ in the one-electron model will keep a certain meaning also in the exact many-electron theory, and many of the semi-empirical discussions and interpretations carried out with the aid of these concepts may hence have a deeper validity than one could expect on the basis of the Hartree-Fock scheme alone. The aim of this approach is hence to give a full justification of band theory within the exact many-electron theory.

In conclusion, let us assume that there exists another normal constant of motion $\Lambda$, which commutes with $H_{op}$ and with $O_{AS}$ say the total spin $(S^2, S_z)$. By introducing the associated set of projection operator $O_\Lambda$ of e.g. type (81), one can now split the antisymmetric basis $\{O_{AS} f_\ell\}$ into a series of subsets $\{O_\Lambda A_{AS} f_\ell\}$, one for each eigenvalue to $\Lambda$. We can now confine our interest to one of these subspaces, which is entirely independent of all the other subspaces, being not only orthogonal but also non-interacting with respect to $H_{op}$ and $\Lambda$. Within this subspace, we can now carry out our partitioning procedure, evaluate the reaction operator $t$, and construct an <u>exact SCF-theory</u> based on a fundamental invariant $\rho$. This is apparently a generalization of the <u>extended Hartree-Fock scheme</u> discussed in Sec. 5 to an exact form. It has already been emphasized that the main part of the correlation error affecting the original Hartree scheme is removed by an inclusion of the

symmetry requirements through the projection operator technique, and only a comparatively small part of the correlation error has then to be treated by true many-particle theory, i.e. by a study of the reaction operator.

The relation between the various types of SCF-schemes has been sketched in Fig. 5.

## 7. CONCLUDING REMARKS

The goal of the many-electron theory is to express the exact wave function in a simple form, e.g. in terms of an expansion which is as rapidly convergent as possible and which contains a dominant term which has a simple physical interpretation. There are particularly four forms which have been used so far [139]:

[139] P.O. Löwdin, Revs. Modern Phys. 32, 328 (1960).

$$\Psi = \sum_K \Psi_K C_K \;; \qquad \Psi = \sum_K (O\Psi_K) C_K \;; \qquad (139)$$

$$\Psi = g \sum_K \Psi_K C_K \;; \qquad \Psi = g \sum_K (O\Psi_K) C_K \,. \qquad (140)$$

Here the first form is an expansion in terms of Slater determinants $\Psi_k$ based on one-electron functions, the second an expansion in terms of projections of determinants $(O\Psi_k)$, whereas the two last forms are similar but contain a "correlation factor" $g = g(r_{12}, r_{13}, r_{23}, \dots)$ which is a symmetric function of the coordinates. The correlation factor was first introduced by Hylleraas [140] and, in connection with crystal theory, it has been pointed out by Krisement [141] that the form $\Psi \approx g D$ is closely connected both with Wigner's [57]

[140] E.A. Hylleraas, Z. Physik 54, 347 (1929).

[141] O. Krisement, Phil. Mag. 2, 245 (1957).

classical theory for the electrons in an alkali metal and Bohm and Pines's [66] plasma model. In the latter, the correlation factor has the following

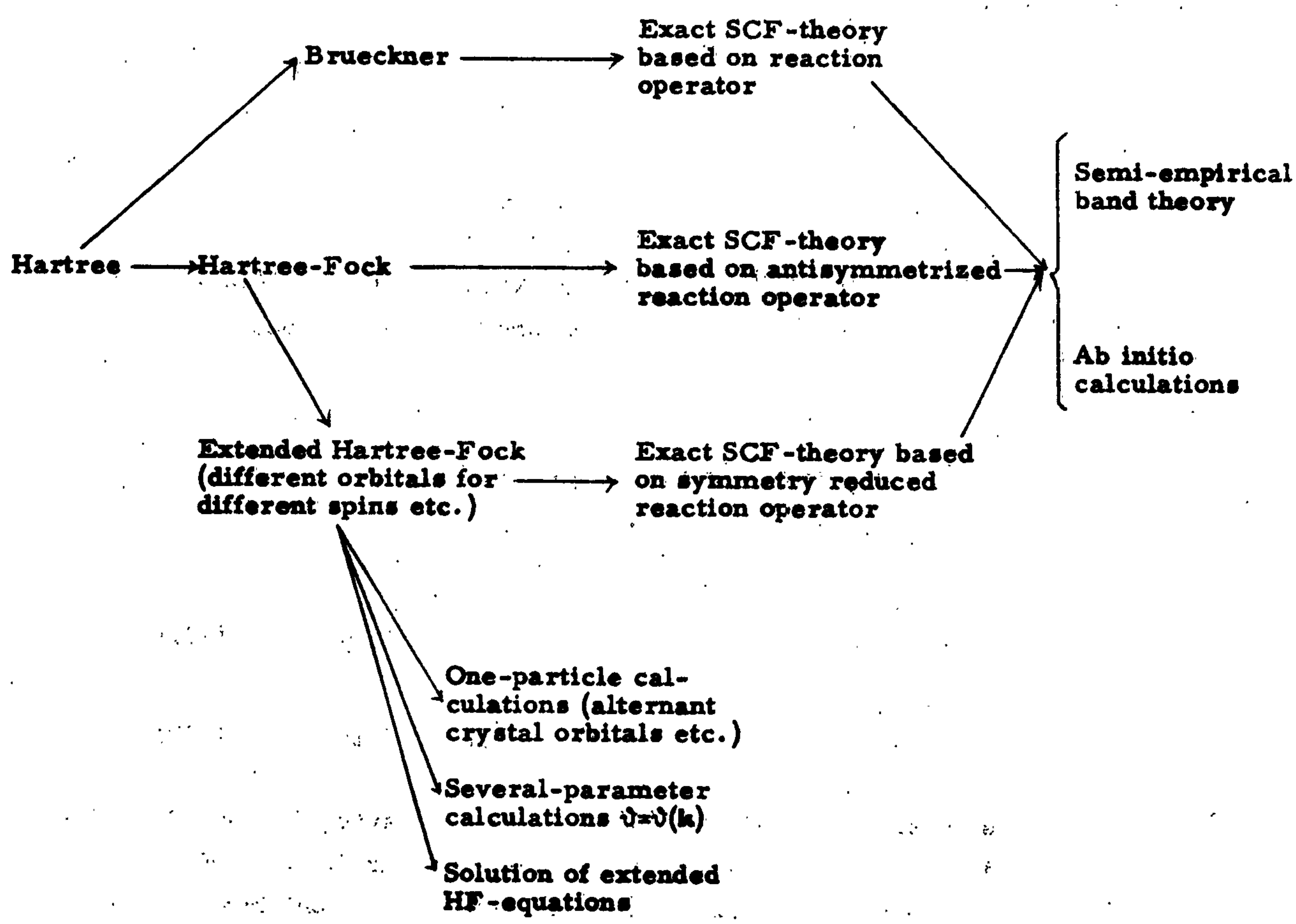


Fig. 5. Schematic survey of the various SCF-schemes which may be utilized in connection with the development of band theory.

form [142]:

$$g = \exp\left\{-\sum_{k<k_c}\sum_{i\neq j} \frac{2\pi e^2}{k^2} \frac{e^{i\mathbf{k}\cdot\mathbf{r}_{ij}}}{\hbar\,\omega_p}\right\}, \tag{141}$$

142) See D. Pines, Solid State Physics 1, 368 (Academic Press, New York 1955), p. 391.

and corresponds physically to the collective motions of the electrons; $k_c$ is the cut-off vector for the plasma oscillations and $\omega_p$ is the plasma frequency. The collective behaviour should, of course, come out as a result of the reaction operator formalism, and it should be mentioned that this problem has recently been studied by Hubbard [143] using infinite-order perturbation theory.

143) J. Hubbard, Proc. Roy. Soc. (London) A240, 539 (1957); A243, 336 (1957); A244, 199 (1958).

We have here confined our interest to the stationary crystal states described by the time-independent Schrödinger equation, but the basic problems in crystal physics could, of course, also be treated by considering the time--dependent wave equation:

$$\mathcal{H}_{op}\Psi = -\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t}. \tag{142}$$

This equation has a solution of the form $\Psi(t) = U(t,0)\Psi(0)$ where the "evolution" operator $U$ is a unitary operator which may be treated by the $\infty$-order perturbation theory systematized by the Feynmann diagram technique [144]. This

144) R.P. Feynman, Phys. Rev. 76, 749, 769 (1949).

approach has not been discussed here at all, but it should be mentioned that important work on the fundaments of crystal theory has recently been made along this line. Actually Hubbard's treatment of the collective motions mentioned above was based on the use of the diagram technique.

In connection with the plasma model, it was also pointed out that there was a short-range correlation effect in the form of a very efficient screening which could simplest be described as a dielectric behaviour of the electrons. This phenomenon and related problems have been particularly studied in the so-called dielectric approximation [145]. Lindhard derives the essential features

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145) J. Lindhard, Kgl. Danske Videnskab. Selskab., Mat.- fys. Medd. 28, 3 (1954); J. Hubbard, Proc. Phys. Soc. (London) A68, 976 (1955); and references 143; P. Nozieres and D. Pines, Phys. Rev. 109, 741, 762 (1958); Nuovo Cimento 9, 470 (1958); J.J. Quinn and R.A. Ferrell, Phys. Rev. 112, 812 (1958); H. Ehrenreich and M.H. Cohen, Phys. Rev. 115, 786 (1959); D.F. DuBois, Ann. Phys. 7, 174 (1959); 8, 24 (1959); A. Klein, Phys. Rev. 115, 1136 (1959); J. Callaway, Phys. Rev. 116, 1368 (1959); D.S. Falk, Phys. Rev. 118, 105 (1960); G.R. Pratt, Phys. Rev. 118, 462 (1960); F. Englert and R. Brout, Phys. Rev. 120, 1085 (1960); and others.

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of this approach starting out simply from the time-dependent SCF-equations, whereas later authors have often utilized the diagram technique and the full $\infty$-order perturbation theory. This method has given particularly important information as to how the electrons in a crystal behave when a weak outer electromagnetic field is applied.

To an experimentalist, the recent development of the quantum theory of the electronic structure of crystals may seem rather complicated, and the question is whether one could find some form of simple connection between the one-electron-model and the exact many-electron theory which could be used in interpreting experiments and constructing semi-empirical theories. In this connection, we would like to direct the attention to the importance of the natural spin orbitals $\chi_\kappa(x_1)$, which diagonalize the first-order density matrix [55]:

$$\Gamma(x_1|x_1') = N\int \Psi(x_1, x_2, \ldots x_N)\, \Psi^*(x_1', x_2, \ldots x_N)\, dx_2 \ldots dx_N, \tag{143}$$

so that

$$\Gamma(x_1|x_1') = \sum_\kappa \chi_\kappa(x_1)\, \chi_\kappa^*(x_1')\, n_\kappa . \tag{144}$$

It may be shown that, if the total wave function $\Psi$ is an eigenfunction to the total translations $\mathcal{T}_\nu$, then the natural spin-orbitals are (or may be chosen as) Bloch functions $\chi_l(\mathbf{k}, x_1)$ associated with the space of the reduced wave vector $\mathbf{k}$, where we have put $\kappa = (\mathbf{k}, l)$. Instead of (144), one obtains

$$\Gamma(x_1|x_1') = \sum_{\mathbf{k}}^{(G)} \sum_{l} \chi_l(\mathbf{k}, x_1)\, n_l(\mathbf{k})\, \chi_l^*(\mathbf{k}, x_1'), \tag{145}$$

and the number of electrons associated with the point $\mathbf{k}$ may now be defined by the expression

$$\begin{aligned} n(\mathbf{k}) &= \left\langle \sum_{i=1}^{N} O_{\mathbf{k}}(i) \right\rangle = \\ &= \int O_{\mathbf{k}}(1)\, \Gamma(x_1|x_1')_{x_1'=x_1}\, dx_1 = \sum_l n_l(\mathbf{k}) \end{aligned} \tag{146}$$

Within the framework of the exact many-electron theory, it is in this way possible to construct a series of concepts which are connected with the $G^3$ points in $\mathbf{k}$-space.

For the kinetic energy $T(\mathbf{k})$ associated with the point $\mathbf{k}$ one obtains for instance

$$\begin{aligned} T(\mathbf{k}) &= \sum_l n_l(\mathbf{k}) \int \chi_l^*(\mathbf{k}, x_1) \frac{\mathbf{p}_1^2}{2m} \chi_l(\mathbf{k}, x_1)\, dx_1 = \\ &= \left\langle \sum_{i=1}^{N} O_{\mathbf{k}}(i) \frac{\mathbf{p}_i^2}{2m} \right\rangle_{\mathrm{Av}}, \end{aligned} \tag{147}$$

and the "effective mass" [146] $m^*(\mathbf{k})$ for the kinetic energy could then be

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146) Compare W. Kohn, Phys. Rev. <u>105</u>, 509 (1957).

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defined by the expression

$$T(\mathbf{k}) = \frac{\mathbf{k}^2}{2\, m^*(\mathbf{k})}\, n(\mathbf{k}) \tag{148}$$

This approach gives hence certain features of the conceptual structure of the theory but, of course, one does not obtain any quantitative results, until one knows the exact wave function $\Psi$ or the associated density matrices. From the experimental point of view, it would be particularly important if one in this way could construct a semi-empirical theory and avoid the formal solution of the Schrödinger equation. The results obtained so far make it likely that such a development may be quite possible.

For a period of about twentyfive years, band theory and valence bond method were applied to the problem of the electronic structure of crystals in their original form. In this review, we have tried to sketch some of the fast development which has occurred in this field during the last decade, the refinement of the conceptual framework and the drive towards higher accuracy in the solution of the Schrödinger equation. Many important results have been obtained, and it seems safe to predict that, during the next decade, still more fundamental results of importance for the understanding of the chemical physics of crystals will be achieved.

## ACKNOWLEDGEMENTS

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